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Polymers and Supercritical Fluids: Opportunities for Vibrational Spectroscopy

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Summary: Supercritical fluids are used for enhanced processing of polymeric materials. Therefore, there is a need to understand how supercritical fluids interact with polymeric materials and how they may modify many facets of process operations. In situ spectroscopy provides a route for understanding and optimising polymer processing with supercritical fluids. In situ spectroscopy probes interactions between supercritical CO_2 and polymers at a molecular level and provides a fundamental understanding of the origin of the plasticising effect of supercritical carbon dioxide on glassy polymers. The changes in polymers subjected to supercritical fluids have been elucidated via in situ ATR(Attenuated Total Reflectance)-IR spectroscopy. The key feature of our new approach is the use of a modified diamond ATR accessory to measure spectra of polymers subjected to high-pressure gas, supercritical fluids or near-critical water. A variety of novel applications for the use of in situ ATR-IR spectroscopy to polymers are described.

Introduction

Recent environmental pressures for the development of "green" technologies have facilitated the broader applications of supercritical fluids in materials processing. Supercritical fluids are attractive for the development of new technologies because of their environmental friendliness and relatively low costs. A particular application of supercritical fluids processing with multiple benefits, is related to the processing of polymeric materials. Here the advantages of supercritical carbon dioxide include its ability to plasticise many glassy polymers and the possibility to "tune" solvent properties of carbon dioxide by varying its density in a broad range. Such "tunability" of the solvent properties is not easily accomplished when using conventional organic solvents. The important difference between traditional polymer plasticisers (e.g. organic solvents) and supercritical CO_2 is that the latter is much easier to remove from

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the polymer materials once the process is complete because CO_2 is a gas at ambient conditions. The plasticising effect of CO_2 on polymers stems from the interaction of CO_2 molecules with the basic sites in polymers, which reduces inter-chain interactions and results in enhanced segmental and chain mobility of the polymer thus providing an enhanced opportunity to process polymers via extrusion, to extract additives or residual oligomers from polymers or to impregnate polymers with doping solutes. Spectroscopy has already played an important role in obtaining evidence for interaction between CO_2 and functional groups in polymers (such as carbonyl groups in PMMA or phenyl rings in polystyrene).[1] This finding has had an impact on polymer modification, synthesis, and polymer processing. CO_2-induced plasticisation of glassy polymers has important implications for modifying polymer morphology. For example, CO_2 can induce crystallisation in certain polymers that occurs when CO_2-induced mobility of polymer chains allows them to rearrange into kinetically favored configurations, thus forming crystallites. Supercritical fluids impregnation of organic dyes into polymers can also be achieved with important implications for environmental benign dyeing of textile materials.[2] In situ FTIR spectroscopy has already been applied to study these processes, and has allowed us to:

- study intermolecular interactions between polymers and carbon dioxide[1]
- detect morphological changes in polymers[3,4] processed with supercritical CO_2
- study kinetics of sorption of CO_2 into PET[5]
- measure partition coefficients[6,7] of different solutes between polymers and CO_2
- reveal interactions between solute and polymer[8,9] under high-pressure CO_2
- measure crystallisation kinetics[10] in polymers subjected to CO_2

In situ spectroscopic studies of supercritical fluids processing requires the use of specially designed high-pressure optical cells.[11,12] These cells are usually constructed for particular purposes and the path length, volume and window materials are chosen at the discretion of researchers. The challenges that need to be overcome in these designs include:

- sealing of the optical windows to be gas leak-proof at high-pressures and over a range of temperatures
- making high-pressure cells safe to minimise the risk of operating under high-pressures
- achieving appropriate path lengths suitable for quantitative analysis

A number of transmission optical cells have been designed for specific applications,[13-17] nevertheless the challenges highlighted above often impose certain experimental limitations. Furthermore, it is very difficult to measure very short path lengths (less than 10 microns) using transmission cells, and the possible elastic deformations of the cell or the window sealing materials may result in changes of the total optical path lengths, thus affecting the quantitative significance of results. It has been recently demonstrated that the use of ATR -IR spectroscopy in measuring the IR spectra of supercritical fluids and liquefied gases appears a good alternative to circumvent the difficulties associated with the use of transmission cells at elevated pressures.[1,18,19] The evanescent wave in ATR-IR spectroscopy measures a very thin layer of the sample that is in contact with ATR crystal. The typical path lengths that the evanescent wave measures in analysing polymeric materials range from 0.1 μm to a few microns (depending on the incident angle and wavelength of light, and refractive indices of ATR crystal and polymeric sample). We have recently pioneered the use of the special ATR-IR cell with a diamond crystal for in situ studies of supercritical fluids. [20,21] The advantages of the use of diamond in such experiments have been recently discussed. These applications of in situ diamond ATR-IR to supercritical fluids include:

- measurement of IR spectra of supercritical CO_2 at pressures up to 300 bar [20]
- study of the diffusion of CO_2 in polymer under high-pressures [20]
- study of the solubility of CO_2 in ionic liquids [22] subjected to high-pressure CO_2
- measurement of IR spectra of near-critical water [21]
- measurement of IR spectra of high-pressure ethane [21]

In this work we outline some new applications of in situ ATR-IR spectroscopy to study:

- sorption of high-pressure CO_2 into polymers
- swelling of polymers under high-pressure CO_2
- impregnation of polymers using supercritical CO_2
- CO_2-induced polymer melting
- CO_2-induced formation of the polymer stereocomplex
- polymers under near-critical water

Results and Discussions

1. Materials and equipment

PMMA (Mw = 120,000) was purchased from Aldrich, UK. Polyethylene glycol (PEG) (Mw = 4,000) was purchased from Fluka, isotactic PMMA and syndiotactic PMMA were supplied by Mr. J. Cabral (Imperial College), Ibuprofen was supplied by Whitehall International, CO_2 was purchased from BOC. ATR-IR spectra were recorded with the use of a Vector 22, Equinox 55 and 66/S FT-IR spectrometers (Bruker, Germany) using MCT and DTGS detectors. The resolution was 2 cm^{-1} in most of the measurements. A modified "Golden Gate" (Specac, Ltd.) ATR accessory with a diamond crystal (incident angle of 45^o) was used. Polymer films were prepared by casting from organic solvent solutions on ATR diamond crystal (for PMMA), or by melting the polymer sample (PEG and PET) placed on the diamond by heating to the polymer melting temperature with subsequent cooling. The polymer sample on the diamond ATR crystal was then covered by the high-pressure enclosure (Figure 1). High-pressure CO_2 was supplied to the cell via syringe high-pressure pump (HiP).

2. Polymer sorption and swelling

First, we describe the application of in situ ATR-IR spectroscopy to measure sorption and swelling polymers under high-pressure CO_2. Poly(methyl methacrylate) (PMMA) was chosen as a test sample because of the availability of literature data[23-25] on the sorption and swelling of PMMA with CO_2. This allowed us to evaluate the feasibility of our new approach. Our previous studies[1,3] of interaction between PMMA and CO_2 also provided us with a good basis for further in situ spectroscopic studies of this system. PMMA, as well as other glassy polymers, absorb significant amounts of CO_2 at elevated pressures. This is accompanied by significant swelling of the polymer matrix. The corresponding values of sorption and swelling determine polymer properties under high-pressures gases, and, therefore, need to be determined over a range of temperature and pressures. Usually, gas sorption is measured gravimetrically while polymer swelling is measured visually.[26,27] The use of in situ ATR-IR spectroscopy allows one to measure polymer swelling and CO_2 sorption into polymer (e.g. PMMA). The idea is based on the fact that while absorption bands of CO_2 dissolved in PMMA provide quantitative sorption data, the absorption bands of PMMA can be used to estimate polymer swelling.

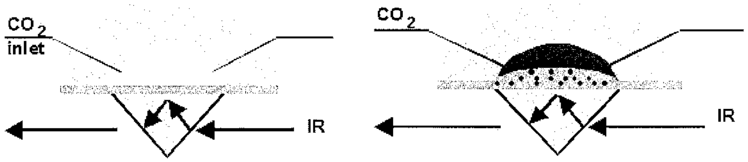

Fig. 1. Schematic view of the ATR-IR high-pressure cell with a sample cast on diamond ATR crystal before (left) and during exposure to high-pressure CO_2 (right).

Figure 1 demonstrates the experimental principle of the method by showing that the density of the polymer layer probed by the evanescent wave changes upon CO_2 sorption into polymer. Thus, the change in absorbance of the PMMA bands provide a measure of the change in PMMA density (and its corresponding volume change) while the absorption bands of the dissolved CO_2 molecules provide data on sorption. Indeed, once the PMMA film has been subjected to CO_2 the following spectral changes were observed: the new bands appeared at ca. 2335 cm^{-1} and 655 cm^{-1} corresponding to the antisymmetric stretching and bending modes of CO_2, and the absorbance of all bands of PMMA decreased (this decrease was achieved rather quickly due to the small thickness of the polymer film which facilitated reaching the equilibrium).

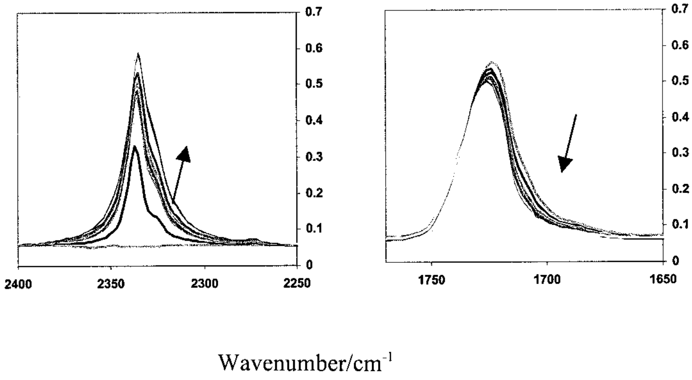

Fig. 2. ATR-IR spectra of PMMA subjected to CO_2 at pressures up to 11MPa (at 42 °C), with the arrows showing changes in the absorbance of the ν_3 band of CO_2 (left) and the $\nu(C{=}O)$ band of PMMA (right) as a function of pressure.

The concentration of the CO_2 can be estimated using the absorbance of the ν_3 band of CO_2 at 2335 cm^{-1}, while the absorbance of the $\nu(C{=}O)$ band of PMMA can be used to estimate PMMA swelling (Figure 2). The decrease of the absorbance of the PMMA $\nu(C{=}O)$ band indicates that the evanescent wave probes less material in the vicinity of ATR crystal compared to the sample at ambient condition. This decrease of the absorbance is a result of polymer swelling which can be quantified using Beer's Law. Thus, using absorbance of the PMMA and CO_2 bands it is possible to determine both PMMA swelling and CO_2 sorption at the same conditions. Figure 2 shows in situ ATR-IR spectra of PMMA recorded at 42 C°, and pressures up to 11 MPa. It is then possible to calculate the swelling and sorption via measured absorbances of these bands using Beer's law and the formulas for effective path length in ATR spectroscopy (detailed description of the corresponding equations and formulas can be found in Ref. 28). It should be noted that all calculations are based on the assumption that the refractive index of the polymer does not change with exposure to CO_2. Strictly speaking this assumption is incorrect since the decrease of the refractive index of polymer could occur due to the gas sorption and corresponding swelling. However, our recent detailed analysis using ATR crystal with two different refractive indices (Diamond and Germanium) allowed us to estimate that the change of the refractive index is relatively small and has actually little effect on the overall data of sorption and swelling.[28] Moreover, the calculated data of CO_2 sorption (presented in Figure 3) and PMMA swelling show good comparison with literature values for sorption data obtained gravimetrically and swelling measured visually for a PMMA/CO_2 system at the same conditions.[29]

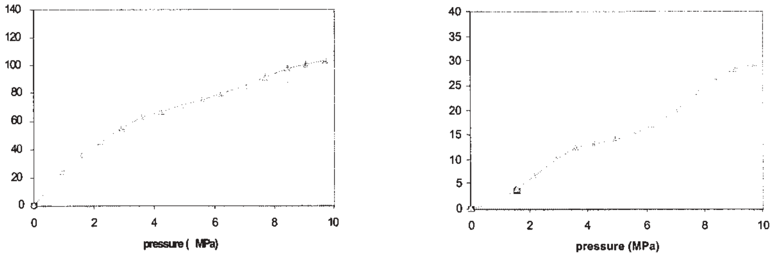

Fig. 3. Concentration of CO_2 in PMMA (in cc (STP) CO_2/g pol) as a function of CO_2 pressure at 42°C and swelling of PMMA (in volume %) as a function of CO_2 pressure at 42°C.

Thus, the in situ ATR-IR method presented here provides a quick and reliable method to measure gas sorption and polymer swelling. It is also important to note an advantage of this method is that there is the possibility to detect the presence of impurities in the gas or polymer (e.g. presence of water) during the experiment via its IR bands while other methods can not detect this. The in situ ATR-IR approach has been used to measure CO_2 sorption and swelling of PMMA at different temperatures,[29] and extended to study polydimethylsiloxane,[28] PEG and biodegradable polymers subjected to high-pressure CO_2 that will be reported elsewhere.

3. *CO_2-induced melting of polymers*

It is known that CO_2 can plasticise glassy polymers reducing the glass transition temperature. In some cases, high-pressure CO_2 can also reduce the melting temperature of polymer.[30,31] In situ spectroscopic studies of CO_2-induced polymer melting would be difficult, if not impossible, due to the associated problems with light scattering of solid polymer and flow of the molten polymer sample. ATR-IR spectroscopy is uniquely suitable to study polymer melting as neither of the above issues would cause any problems if the evanescent wave probes the polymer placed on the ATR crystal in the arrangement similar to the one shown in Figure 1. It has been reported that high-pressure CO_2 can reduce the melting temperature of poly(ethylene glycol) PEG for different molecular weights. Such a reduction of the polymer melting temperature may have important implications since it would allow the viscosity of the polymer to be significantly decreased without additional heating which could make processing easier at milder temperatures.

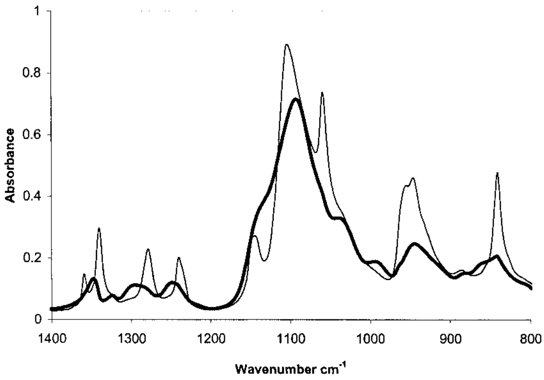

Fig. 4. ATR-IR spectra of PEG at 25 °C (thin line) and during exposure to 60 bar of CO_2 (thick line).

Figure 4 shows the ATR-IR spectra of PEG and PEG subjected to high-pressure CO_2 at temperature of 25 °C. Dramatic changes occur at 60 bar pressure of CO_2 with a shift and broadening of all spectral bands of PEG. Similar changes have been observed in the IR spectrum of PEG when it was heated above its melting temperature of 47 °C at atmospheric pressure. This example demonstrates that in situ ATR-IR spectroscopy allows one to monitor melting of polymer induced by high-pressure CO_2. This approach can be applied to a range of polymers with different molecular weights since spectroscopic changes are not limited by polymer viscosity. Applications of in situ ATR-IR spectroscopic monitoring to the CO_2-induced melting of PEGs is especially interesting because this polymer is used in pharmaceutical applications, and thus CO_2-assited processing of this polymer at reduced temperatures may be beneficial.

4. In situ ATR-IR monitoring of impregnation of polymer from supercritical fluid solution

Impregnation of bioactive substances into molten polymer would proceed faster than into solid polymer and would also result in homogeneous distribution of a solute in polymer solution. There is an additional advantage in the case of CO_2-induced melting of polymer: depressurising of the system would result in CO_2 leaving the polymer matrix, polymer reverting to its solid state thus "freezing" impregnated solute molecules within the matrix before they are allowed to re-crystallise. Figure 5 shows an example of the use of in situ ATR-IR spectroscopy to observe the impregnation of ibuprofen into PEG.

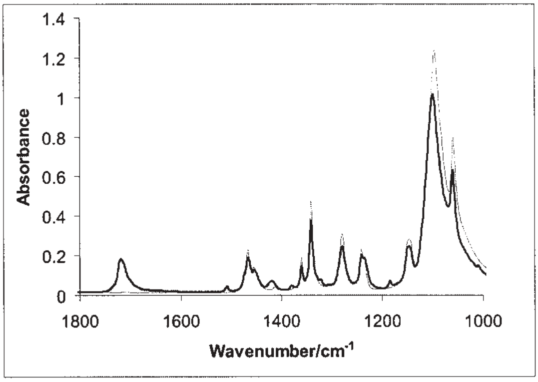

Fig. 5. ATR-IR spectrum of PEG before and after (thick line) it has been subjected to solution of ibuprofen in supercritical CO_2. Bands marked with arrows correspond to the bands of ibuprofen molecules impregnated into PEG.

The spectra presented in Figure 5 clearly show the IR absorbance bands of ibuprofen impregnated into PEG from CO_2 solution. The action of CO_2 here is threefold: to depress the melting point of PEG, to dissolve ibuprofen and to act as a carrier of ibuprofen into molten PEG. It should be noted that ATR-IR in situ spectroscopic monitoring of the impregnation process can also be used for polymers where melting does not occur, such as supercritical fluid impregnation of ibuprofen into polyvinylidene pyrrolidone (PVP).[32] In this case the use of ATR-IR in situ approach has allowed the molecular state and crystallinity of ibuprofen molecules in PVP matrix to be elucidated, thus providing control of solid dispersions of drug in polymer matrix.

5. CO_2-induced formation of stereocomplex of PMMA

Recently, the use of supercritical CO_2 has been demonstrated in the formation of a crystalline stereocomplex between isotactic (it-) PMMA and syndiotactic (st-) PMMA.[33,34] This has been studied by means of DSC and WAXS as a function of CO_2 pressure and temperature, it-PMMA/st-PMMA mixing ratio, and PMMA molecular weight. In these studies it has been shown that the amount of the stereocomplex formed by high-pressure CO_2 was higher than that induced by heating, and that such crystalline stereocomplexes contribute to the superior morphology of the microcellular foams that were obtained by treatment of PMMA with high-pressure or supercritical CO_2. It has been assumed that the stereocomplex formation has been induced by enhanced mobility of PMMA. The dynamics of ester methyl group in PMMA stereocomplex has been demonstrated in a neutron scattering study.[35] Increased segmental mobility of ester side units of st-PMMA has been observed via in situ ATR-IR spectroscopy in a CO_2-plasticized PMMA.[3] Our previous spectroscopic study has demonstrated that the plasticizing effect of CO_2 in PMMA is the result of the ability of CO_2 molecules to interact with the carbonyl groups in PMMA, this interaction has been suggested to be of the Lewis acid-base type.[1] These studies demonstrated how the effect of high-pressure CO_2 mimics the effect of heating the polymer. Thus, with the hindsight, it is not surprising that supercritical CO_2 assists the formation of stereocomplex between st-PMMA and st-PMMA. Mizumoto et al.[33] have recently studied the enthalpy changes of stereocomplex it-PMMA/st-PMMA as a function of CO_2-treatment time. DSC measurements has shown that the rates of the stereocomplex formation induced by high-pressure CO_2 treatment were faster than those induced by heating polymers above Tg. The results are very interesting, but, unfortunately, the analysis of the samples was done after the high-pressure treatment. Given the potential of supercritical CO_2-induced formation of the stereocomplex it is important to monitor the process in situ. ATR-IR spectroscopy of the cast polymer films, as described above, offers the possibility to monitor the process of the stereocomplex formation in situ as a function of temperature.

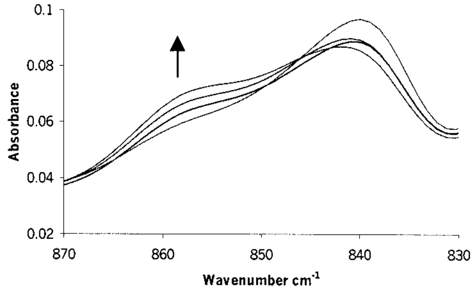

Fig. 6. ATR-IR spectra of mixture it-PMMA/st-PMMA subjected to 100 bar of CO_2 at 40 °C as a function of time.

Figure 6 shows ATR-IR spectra in the spectral region of PMMA sensitive to the formation of the stereocomplex for the cast film of st-PMMA/it-PMMA subjected to 100 bar of CO_2 at 40 °C as a function of time. The increase in absorbance of the band at 860 cm^{-1} (due to CH_2-rocking vibrations in the st-PMMA with *trans-trans* backbone conformation) with time indicates an increase in amount of the forming stereocomplex induced by high-pressure CO_2. This example shows the potential of the in situ ATR-IR approach presented here for monitoring this process. The detailed analysis of this process will be presented elsewhere.

6. *Polymers in near-critical water*

Currently there is increasing interest in using another supercritical solvent - supercritical water, which is an inherently benign solvent. However, the critical temperature of water (374 °C) is relatively high and at these conditions water is quite an aggressive solvent, thus special materials are often required for construction of reaction vessels. However, near-critical water at temperatures of 200-300 °C also has interesting properties. For example, the dielectric constant of water at these temperatures drops to 20 compared with 80 at ambient temperature. There are significant research efforts to utilise near-critical water as a solvent for acid-base catalysed reactions. Another potential application of near-critical water involves polymer recycling since depolymerisation and decomposition of many polymers in near-critical water occurs at elevated temperatures.[36-38] Recent observation of decomposition of polymers into monomers, when subjected to near-critical water, has demonstrated that it is necessary to study these phenomena via in situ analysis. However, infrared spectroscopic study of aqueous solutions is challenging due to the strong infrared absorption of water. ATR-IR spectroscopy proved to be useful due to its inherent ability to probe a very short pathlength in the micrometer range. The short pathlength in a single reflection ATR utilising diamond crystal provides the possibility to measure polymers subjected to near-critical water in situ. Therefore, we were able to measure spectra of polymers cast on diamond under near-critical water conditions. The ATR-IR spectra of poly(ethylene terephthalate) (PET) subjected to liquid water at elevated temperatures have been measured. As a first step, we have observed in situ, for the first time, changes in the ATR-IR spectra of PET subjected to near-critical water at 220 °C. Spectral changes (not illustrated) provide evidence for the formation of terephthalic acid and ethylene glycol. Although the formation of these compounds as a results of hydrothermal decomposition of PET was reported before,[39-41] including spectroscopic study[42] of hydrolytic degradation of PET at 90 °C our approach allows us to monitor the kinetics of PET decomposition in near-critical water in situ and potentially to optimise conditions for this process. This is ongoing research and detailed results will be reported elsewhere. The opportunities of in situ high-pressure ATR-IR monitoring of polymer decomposition in near-critical water will have a strong impact on polymer recycling and waste minimisation. Since near-critical water processing has clear economic and environmental benefits this would aid in the development of sustainable technology and our spectroscopic approach may facilitate the broader use of near-critical water and supercritical fluids.

Conclusions

The in situ ATR-IR spectroscopic approach described here provides an opportunity to study interactions between polymers and supercritical fluids. This method allows one to measure simultaneously gas sorption into polymer and polymer swelling under high-pressure conditions. This information obtained in situ is required for optimisation of polymer processing with supercritical fluids. The in situ spectroscopic approach also offers the possibility to study the mechanism of gas sorption in polymers via monitoring of gas diffusion and has a number of advantages over volumetric and gravimetric techniques. In addition, we have demonstrated how the in situ ATR-IR method allowed us to observe supercritical CO_2-induced melting of poly(ethylene glycol) and to monitor impregnation of pharmaceuticals into molten polymer. Such spectroscopic information is important in the development of supercritical fluid processing of polymer/drug formulations and would be challenging to obtain by in situ transmission spectroscopy. This in situ ATR-IR spectroscopic method has also been applied to study the formation of stereocomplex of PMMA induced by high-pressure CO_2. It has been shown that the method has good potential for studying polymers subjected to near-critical water and to monitor in situ decomposition of polymers under these conditions. This novel in situ ATR-IR spectroscopic approach will lead to knowledge that is required for optimisation of polymer processing under hydrothermal conditions with a good potential for sustainable technology.

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