NMR Studies on the Properties of Polymers in Supercritical CO$_2$

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Using NMR spectroscopy and NMR imaging, the behaviour of polymers in supercritical CO$_2$ (sc-CO$_2$) using a custom-made cell designed from poly(ether ether ketone) (PEEK) has been observed. The mechanism of swelling of polymers in sc-CO$_2$ and the overall effects of sc-CO$_2$ on the transport properties of both small and large molecules has been studied. We report on the swelling characteristics of radiation-crosslinked PDMS rubber and semicrystalline polymers. The morphology of blends of poly(ethylene) and poly(styrene) was studied using raman microprobe imaging and solid-state MAS NMR spectroscopy.

Introduction

It is well known that the solubility of most polymers in sc-CO$_2$ is very poor, however, the degree of swelling of many polymers is high in this solvent. Extensive research has been applied to measuring the extent of swelling of a polymeric substance upon dissolution of sc-CO$_2$. We have shown that some polymers, in particular crosslinked PDMS, can be swollen quite dramatically, and that this solubility of sc-CO$_2$ in polymers can have a significant effect on the overall interaction between co-polymers in a polymeric blend formed in sc-CO$_2$.

Numerous authors have utilised different methods of quantifying polymer swelling due to supercritical CO$_2$ sorption [1,2,3]. Most of these methods are simple and measure the linear expansion of the polymer. Indeed, DeSimone et al. [3] visually measured swelling of PDMS in a single dimension using a high-pressure view cell. In a similar case, Wynne et al. [2] used a linear variable differential transformer (LVDT) method to monitor linear expansion of the polymer. NMR imaging is a particularly useful method of quantifying the swelling capability of sc-CO$_2$ on different polymers under varying conditions. The imaging capabilities and resolution of the probe provided an *in-situ* magnetic resonance image of the swelling polymer in the CO$_2$ medium.

Ever since the first high-pressure probe of Benedek and Purcell [4] in 1954, the following five decades exhibited an increasing interest in high pressure NMR. Our high-pressure NMR experiments were achieved using a home-built pressure cell slightly modified from an original design of Wallen et al. [5]. The cell, designed from poly(ether ether ketone) (PEEK), is capable of withstanding pressures of greater than 600 bar and is regularly used at 300 bar. The advantage of this high-pressure method, compared to that originally used by

Purcell and Benedek [4] and subsequent researchers, is the ability to use the PEEK cell in any standard 10 mm resonator. In this way, NMR imaging and solid-state experiments could be performed using the same cell with minimum alterations to the original design.

Understanding of the mechanisms and processes involved in polymer swelling leads to the study of small molecule diffusion into these polymers. McCarthy and Watkins [6] originally developed the idea of using supercritical carbon dioxide as a solvent, and swelling agent, for the infusion of a monomer into a polymeric substrate. This was based upon two separate patents published around the same time [7,8]. A number of researchers have shown that it is possible to develop polymer blends with unique properties, by using supercritical carbon dioxide as both a permeant, and hence a swellant, and as a solvent for the monomer species [9-13]. These authors have also suggested that there is much greater miscibility between the two polymeric components in the blends than is observed using conventional methods of synthesis. Whilst the theories explaining this greater extent of mixing of the polymers are fairly intuitive, that is the greater swelling of the polymer substrate allows greater mixing than under normal conditions, very little quantitative evidence of this improved miscibility has been described.

In this paper, we present NMR images highlighting the enhanced swelling of polymers under supercritical conditions, particularly in radiation-crosslinked PDMS. We also present NMR imaging data collected for a model monomer (ie. styrene) infusing into a semicrystalline polymer substrate (ie. LLDPE). The well known immiscibility of these two polymers in a conventional blend serve as a good test for the predicted improvement in miscibility when blended under supercritical conditions. We present measurements of domain sizes using raman microprobe spectroscopy and solid state NMR and compare blends formed in sc-CO2 and at standard pressure.

Materials and Method

LLDPE (DOW 2056) was processed as received. The styrene monomer was obtained from Sigma Aldrich and was purified by firstly passing through an Al_2O_3 column to remove the tert-butylcatechol inhibitor, followed by distillation in a micro-distillation system under vacuum. The monomer was then stored at $- 4$ ^{o}C for up to two weeks. The AIBN was obtained from Sigma Aldrich and recrystallised three times from methanol and stored at $- 4$ ^{o}C away from light. Dow Corning SFD-5 PDMS fluid was γ-irradiated using a 220AECL ^{60}Co facility for 48 hours in air at room temperature. This was found to be well above the gel dose for the sample. Blends were formed by soaking the LLDPE film in styrene/AIBN (50 Vol%) in sc-CO$_2$ at 150 bar and 40 ^{o}C for various times, followed by polymerisation at 80 ^{o}C and 80 bar.

NMR Imaging was performed on a Bruker AMX300 spectrometer. The images were collected using a spin echo, three-dimensional, SE3D pulse sequence. Each image consisted of 128 x 128 x 8 voxels and had a field of view of 0.5 x 0.5 x 5 cm to give a slice thickness of 6.25 mm and an in-plane resolution of 39 microns.

Raman microprobe spectroscopy was undertaken on a Renishaw System 1000 Raman Microprobe spectrometer equipped with a He-Ne laser operating at 632.8 nm. The microscope was an Olympus MD Plan microscope with a 50x objective lens giving a focus spot size of

approximately 1 micron. Images were collected using 1 micron steps through the cross-section of a pre-cut polymer sample that had been securely mounted on the microscope stage.

Solid-state magic angle spinning nuclear magnetic resonance was performed on an MSL 300 spectrometer operating at 300.13 MHz for ^{1}H. Values of ^{1}H $T_{1\rho}$ relaxation times were determined from the exponential decay of magnetization during the spin locking pulse used prior to ^{1}H-^{13}C cross-polarization. Domain sizes were estimated by modelling relaxation decays using software that coupled measured ^{1}H $T_{1\rho}$ values with spin diffusion parameters.

Conclusion

Swelling of the polymers was monitored using NMR imaging techniques. The sample cell was pressurised from the CO_2 bottle (50 bar) and left to equilibrate for 5 minutes. An image was taken and then the sample was pressurised in 50 bar steps with images taken following the 5 minute equilibration time. Figure 1 depicts images gathered for a crosslinked PDMS sample at standard temperature and pressure and at 250 bar. Substantial swelling could be observed with an overall volume increase of about 40 % at this pressure.
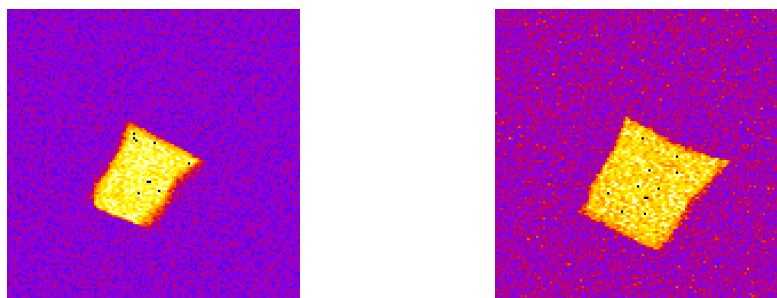

Figure 1: Cross-section of NMR images of the PDMS sample in the high-pressure NMR cell. Illustration on left is at 1 bar, 45°C whilst the one on the right is at 300 bar, 45°C.

The interaction parameter for sc-CO_2 was calculated as a function of pressure by comparison of this swelling data with that of a conventional solvent, toluene, and by application of the Flory-Huggins equation:

$$\chi = - [(G_e/RT)v_1 v_2^{1/3} + \ln(1-v_2) + v_2] / v_2^{2}. \tag{1}$$

Figure 2 highlights the progressive decrease in the interaction parameter as the pressure is increased from room pressure to 300 bar at a constant temperature of 45°C. This decrease is indicative of an improvement in the solvent quality.
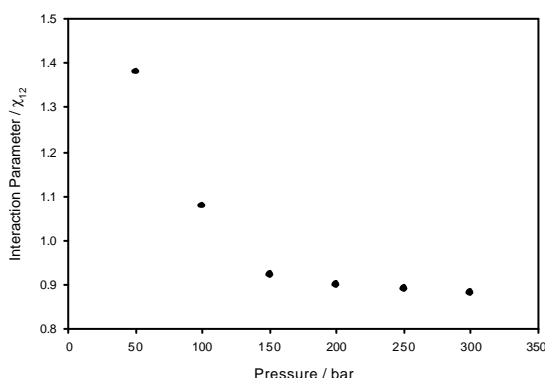

Figure 2: Interaction parameter for sc-CO_2 and crosslinked PDMS versus pressure.

This improvement has been well established by numerous authors and is undoubtedly due to the increase in density of the solvent with pressure and hence an increase in the solubilizing power of the CO_2. The apparent limiting value of the interaction parameter with pressure is also a reflection of the density and solubility properties of CO_2 with the largest change occurring around the critical point. The limiting value for the interaction parameter was 0.88 for crosslinked PDMS suggesting that sc-CO_2, even at the highest pressure measurable using our cell, is a relatively poor solvent for PDMS.

Improved transport properties of small molecules into polymeric substrates when dissolved in sc-CO_2 were observed. The diffusion of styrene monomer into poly(ethylene) was observed by NMR imaging. Figure 3 shows the diffusion profile of the monomer into poly(ethylene) film at standard pressure and in sc-CO_2.
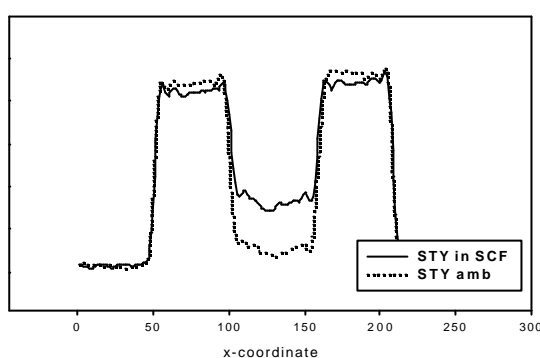

Figure 3: Profile taken from NMR images showing styrene diffusion into LLDPE at 1 bar (3 hrs, 45°C) and at 250 bar (30 minutes, 45°C).

Similar profiles were observed for a 30 minute soak in sc-CO_2 compared to a soak of 3 hours at ambient pressure. Thus, the supercritical fluid increases the role of mass transport of the styrene monomer considerably by swelling the polymeric substrate and dissolving the monomer giving it the gas-like diffusivities characteristic of a supercritical fluid. The supercritical fluid, then, increases the uptake of styrene into the LLDPE substrate.

Raman microprobe spectroscopy was used to measure the spatial distribution of the polystyrene within the polymer blends. It has been shown that the resolution of the raman microprobe method is 2 microns [14], hence for poly(styrene) domain sizes larger than two microns, that is gross phase separation, discrete intensity peaks would be observed on a cross-sectional map. Conversely, domain sizes below 2 microns would result in a featureless map. Figure 4 shows raman maps obtained through the cross-sections of a blend formed in sc-CO_2 and a blend formed at ambient pressure. The z-axis denotes raman intensity, or concentration of styrene at a particular point on the map. Both graphs have the same scale, and it is evident that the blend formed at ambient temperature has discrete areas of concentrated poly(styrene). This immiscibility has been well established in the past, where blends utilising poly(styrene) and poly(ethylene) require addition of a suitable compatibiliser if greater miscibility is desired for a given application. The blend formed in sc-CO_2, however, shows a featureless map suggesting that there is greater miscibility between the two components of the blend in this case.
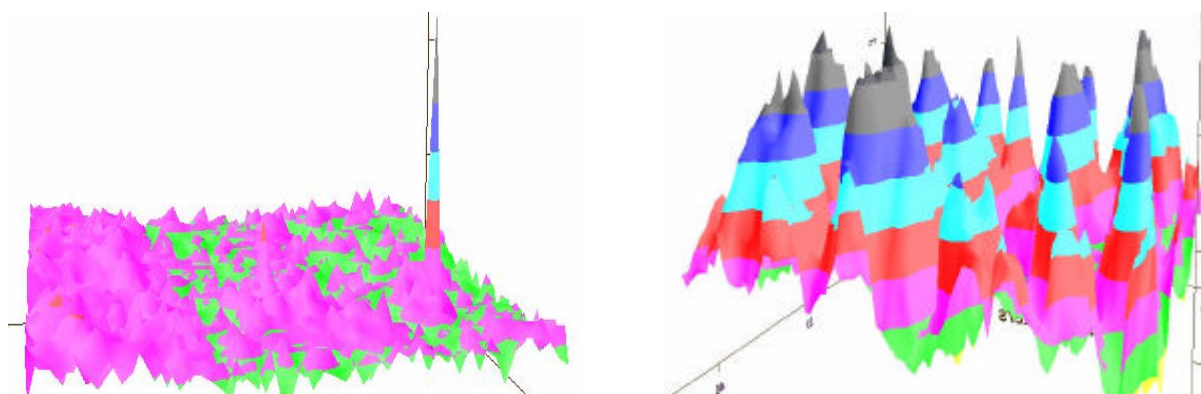
Figure 4: Raman map of blend formed in sc-CO_2(left) and blend formed at ambient pressure (right). Z-axis denotes raman intensity of polystyrene.

A convenient method of measuring domain sizes of the order of tens of nanometres is solid-state NMR [15]. The arrangement of the poly(styrene), amorphous poly(ethylene) and crystalline poly(ethylene) phases can be determined by changes in the spin-lattice relaxation times after blending. By modelling this data with a computer generated "ideal blend", it was possible to determine the average domain sizes of the poly(styrene) within the poly(ethylene). Theoretical relaxation times (Table 1) were calculated for blends of poly(styrene) and poly(ethylene) using realistic NMR parents.

It was observed that as the degree of mixing, or miscibility, increases (smaller domains), averaging of the relaxation times occurs. Comparison of the values of relaxation times determined experimentally with values calculated theoretically provides estimates of the average domain sizes for the two types of blends (Table 1). Clearly the results suggest more intimate mixing in the blend formed in sc-CO_2.

	Intrinsic ^{1}H T1$_r$	Experimental ^{1}H T1$_r$	Modelled ^{1}H T1$_r$	Domain Size
PSTY	**8 ms**	**4.91 ms**	**4.95 ms**	**4 nm**
LLDPE	**1 ms**	**0.6 ms**	**1.04 ms**	
PSTY	*8 ms*	*9.4 ms*	*8 ms*	*> 100 nm*
LLDPE	*1 ms*	*1.2 ms*	*1 ms*	

Table 1: Modelled domain sizes for blends formed in sc-CO_2 (bold) and blends formed at ambient pressure (italics).

The raman and NMR results are in good agreement, suggesting overall that there was a significant increase in miscibility if the blends were formed using sc-CO_2 as opposed to experiments under ambient conditions. It has been widely shown in the literature by mechanical testing that favourable molecular interactions must have been occurring in blends formed using sc-CO_2, since the mechanical properties of a blend formed in sc-CO_2 showed significant improvement over those of a corresponding blend formed at ambient pressure. The results of the measurements of mechanical properties strongly suggest greater miscibility between the blend components. Nonetheless, the absence of a quantitative assessment of domain sizes in the literature was noticeable. Scanning electron micrographs are commonly used to prove miscibility, however these are often marred by artefacts and require extensive

staining of one species. Our results represent the first quantitative assessment of the improved miscibility in these blends by a means other than electron microscopy.

The improved miscibility, as detected by NMR, suggests that there is much more intimate mixing of the two components in blends formed in sc-CO_2. This is probably the result of the massive swelling of the substrate polymer, allowing greater diffusion between the entangled polyethylene chains in the amorphous regions. Similarly, the greater diffusivity of the supercritical carbon dioxide would accomplish much better penetration between these chains. The effect upon depressurisation would, then, be a much more homogeneous polymer blend, as is observed. Understanding of the swelling characteristics, and these intimate interactions on the nanometre scale are important then, if the chemistry used in this simple system is to be transferred to a more complicated, multiphase system. It is obvious that both imaging and solid-state NMR have an important role to play in understanding the chemistry involved in processing in sc-CO_2.

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