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Solubility of Supercritical Carbon Dioxide in Polycaprolactone (CAPA 6800) at 313 and 333 K

Gary A. Leeke*

Centre for Formulation Engineering, Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K.

Jiangou Cai

Chemical Engineering Research Centre, East China University of Science and Technology, Shanghai 200237, China

Mike Jenkins

Metallurgy and Materials, School of Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K.

The solubility of carbon dioxide in polycaprolactone (CAPA 6800) was measured at (313 and 333) K between pressures of (80 and 200) bar. Data were obtained using a static method that allowed saturation of the polymer with CO_2 under the experimental conditions.

Introduction

Polycaprolactone (PCL) is a semi-crystalline, thermoplastic, aliphatic polyester.[1] It is biodegradable in that it can be degraded by hydrolytic mechanisms in a physiological environment. This property has resulted in a wide range of biomedical applications for the polymer. These include its use as a matrix for drug delivery systems and cell microencapsulation.[2] PCL can be processed using a wide range of methods, although films produced by blowing are often tacky and as a result, compression moulding from pellets is usually employed.[3] The high decomposition temperature of 350 °C does enable PCL to be extruded.[4] Solvent casting can also be used, but this method often utilizes high volumes of solvent and results in a material containing organic solvent residues, which may be difficult to remove.[5] Fiber bonding, particulate leaching, and melt molding are also employed to produce both microparticles and polymeric scaffolds for biological applications.[6]

An alternative approach to these conventional manufacturing methods is supercritical fluid (SCF) processing. The use of SCFs is particularly important when the viscosity of the bulk polymer is relatively high, as in the case of high molecular weight polymers. The relatively high viscosities that result from high molecular weights require correspondingly high temperatures to facilitate processing, although elevated temperatures can often lead to thermal degradation and deterioration in physical properties of the material being processed.[7] In cases such as these, SCFs can facilitate processing by acting as a solvent, reducing the intermolecular interactions and increasing the chain separation, in effect acting as a molecular lubricant.[8] Several workers have reported the use of supercritical CO_2 as a blowing agent in the preparation of PCL foams.[9−11] Characterization of the effect of processing with supercritical CO_2 can be achieved by the use of the Flory−Huggins method. However, this analytical method relies on the measurement of the solubility of CO_2 in PCL, and at present there is very limited published data on this solubility. Cotugno et al.[12] have reported the solubility of CO_2 in PCL at temperatures of (343 to 358) K and at pressures up to 65 bar. Their work was carried out at temperatures above the ambient pressure melt temperature (T_m) of PCL CAPA 6800, which was recorded at 331 K. To determine the extent of the plasticization effect on the polymer by adding CO_2, it is necessary to undertake solubility measurements below and in the vicinity of the T_m. Therefore, this paper is the first to report solubility data of CO_2 in PCL at temperatures of (313 and 333) K and pressures up to 200 bar. A reduction in temperature is advantageous for the processing of thermally labile biocompounds that can be incorporated during the processing stage; consequently, supercritical processing of polymers below the T_m requires much higher applied pressures than those used by Cotugno et al.[12] Data were obtained using a static method that allowed saturation of the polymer with CO_2 under the experimental conditions.

Experimental Section

Materials. Polycaprolactone (CAPA 6800) was supplied by Solvay (U.K.) and was used without further purification. The structure of the repeat unit of PCL is shown in Figure 1. Prior to use, the polymer samples were vacuum-dried at 38 °C for 48 h. Liquid carbon dioxide was obtained from BOC, CP grade, and had a given purity of 99.995 %. The ambient melt temperature of PCL was determined by DSC (Perkin-Elmer Pyris 1) to be 332 K. The number-average molecular weight was 69 000 ± 1500, the weight-average molecular weight was 120 000 ± 2000, and the polydispersity index was equal to 1.74.

Equipment. The apparatus used to determine the high-pressure CO_2 solubility data is shown in Figure 2. The equilibrium cell (2) had an internal volume of 100 cm^3 and was charged typically with (5 to 8) g of PCL flakes. It was maintained at a constant temperature by a covered heated water bath (5). Liquid carbon dioxide was passed through a chiller, compressed, heated to the desired conditions, and directed to the equilibrium cell. The carbon dioxide feed entered the cell at the opposite end to the sampling position. This minimized

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* Corresponding author. Tel: +44 121 414 5351. Fax: +44 121 414 5324. E-mail: G.A.Leeke@bham.ac.uk.

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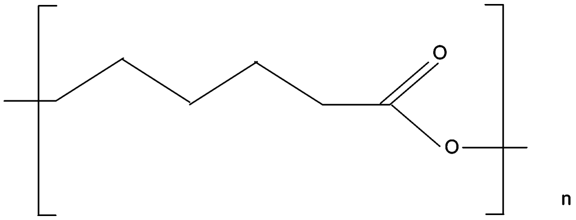

Figure 1. Repeat unit of polycaprolactone.

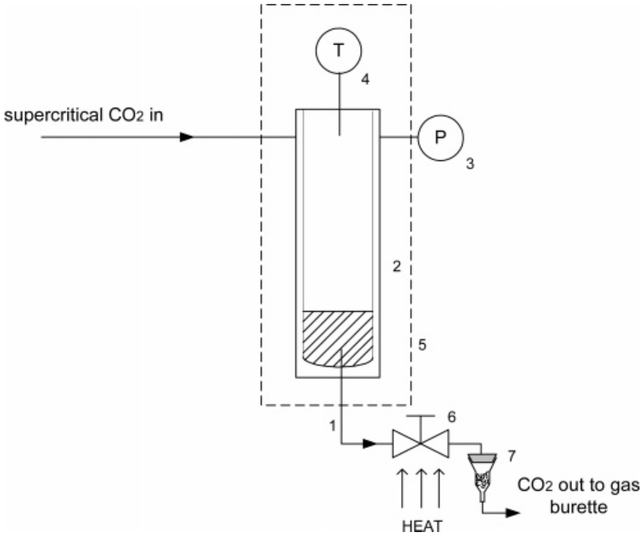

Figure 2. Apparatus used to measure high-pressure liquid-phase data: 1, dip tube for sampling; 2, equilibrium cell; 3, pressure transducer; 4, thermocouple; 5, temperature-controlled water bath; 6, micro-metering expansion valve; 7, collector.

any mixing of fresh make-up carbon dioxide, which was required to maintain the equilibrated pressure during sampling, with the equilibrated mixture being sampled. The system was kept for up to 27 h (24 h typical) at a steady state to allow CO_2 to diffuse into and equilibrate with the PCL. This optimum time was predetermined from repetition of experiments. In addition, any undissolved carbon dioxide present in the polymer-rich phase would be transported to the CO_2-rich vapor phase. After this time, the polymer-rich phase was sampled. The pressure was measured by a pre-calibrated transducer (Druck, U.K.) which had an uncertainty of 0.014 %. The temperature was measured by a K-type thermocouple, which had an uncertainty of ± 0.1 °C.

Sampling Procedure. Samples were withdrawn through a dip tube (1) submerged in the PCL-rich phase and depressurized across a heated micro-metering valve (6; Hoke 1315G4Y) located at the base of the equilibrium cell. At the conditions reported, the viscosity of PCL had been sufficiently reduced to enable the PCL + CO_2 mixture to flow along the sample tube. Due to the nature of the system the volume of CO_2 in the PCL phase was small (i.e., a large mass of PCL was present), a gas burette filled with calcium chloride confining solution was used to measure the volume of gas. Due to the low vapor pressure of PCL, the mass trapped in the glass collector was determined gravimetrically using an *AND* HR-200 balance which had a reproducibility of ± 0.001 g. This would have given an uncertainty of 2.2 % in the sample mass collected. Following sample collection, any PCL present in the internals of the valve at ambient conditions was usually accounted for by washing the valve internals with a swab of predetermined mass soaked in dichloromethane. Following solvent evaporation, the mass of the polymer was determined gravimetrically using a balance with an accuracy of 0.00001 g (Mettler MT5), which would have led to an uncertainty of 0.23 % in the mass collected. The mass of PCL here typically represented less than 7 % of the total mass.

Table 1. Liquid-Phase Data for PCL (CAPA 6800) + CO_2

$T = 313$ K		$T = 333$ K	
nominal P/bar	g of CO_2/g of PCL	nominal P/bar	g of CO_2/g of PCL
80	*a*	80	0.0293
100	0.8710	100	0.4987
125	2.4238	125	1.0816
153	2.8319	153	1.3711
200	3.2044	200	1.6379

[a] No data collected.

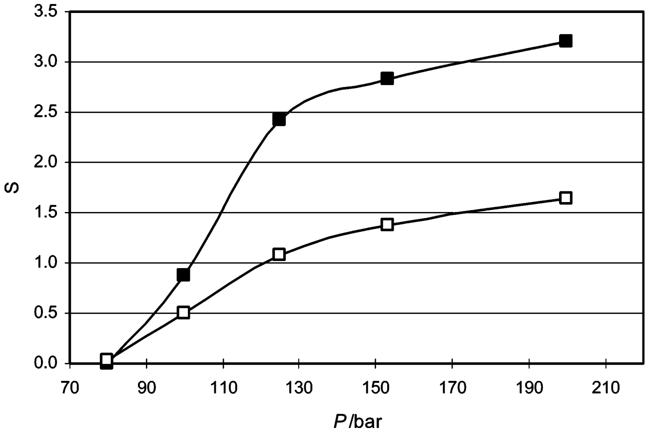

Figure 3. Solubility of CO_2, S as g of CO_2/g of CAPA in PCL: ■, 313 K; □, 333 K.

Results and Discussion

Liquid-phase data for the PCL + CO_2 system were measured at (313 and 333) K and between pressures of (80 to 200) bar. The authors refer to an earlier publication for proof of the reliability of the apparatus and methodology employed.[13] The results at the experimental conditions are shown in Table 1 and are expressed in g of CO_2/g of PCL. The solubility data are the average of several measurements at each pressure. The probable error of each result (r) and the probable error of the mean of the results (r_o) were calculated from

$$r = t\sqrt{\frac{\sum \nu^2}{n-1}} \tag{1}$$

$$r_o = \frac{r}{\sqrt{n}} \tag{2}$$

where υ is the variance, n is the number of the datum point, and t is a numerical value dependent on n.[14] The worst probable error of each individual result did not exceed 0.117 g of CO_2/g of PCL at 200 bar and 313 K. This represented a 3.7 % variance from the mean. The worst percentage deviation from the mean solubility was at 100 bar and 313 K, which was calculated to be 5.4 %, but as the solubility here is lower, any percentage error is magnified. Similarly, the probable error for this test was calculated to be 0.047 g of CO_2/g of PCL. For all tests the probable error of the mean was no greater than ± 0.052 g of CO_2/g of PCL.

It can be seen from Figure 3 that the solubility of CO_2 increases with pressure and decreases with temperature. At the higher temperature, less CO_2 is required to reduce the intermolecular interactions and increase chain separation to enable the polymer to become plasticized. Figure 3 also shows that CO_2 has no recorded solubility below 80 bar at the temperature conditions. This is highlighted by the absence of a solubility value obtained at 313 K in Table 1. The experimental method relies on the plasticization of the polymer by CO_2 dissolution at the equilibrium condition to enable it to flow into the sampling system. It is therefore apparent that the plasticization effect is undetectable below 80 bar at these temperature conditions. An increase in temperature would enable the polymer to become plasticized at pressures below 80 bar.

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