

Effect of compressed CO₂ on crystallization and melting behavior of isotactic polypropylene

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Abstract

Compressed gases such as CO₂ above their critical temperatures provide a highly tunable technique that has been shown to induce changes in phase behavior, crystallization kinetics and morphology of the polymers. Gas induced plasticization of the polymer matrix has been studied in a large number of polymers such as polystyrene, and poly(ethylene terephthalate). The knowledge of polymer–gas interactions is fundamental to the study of phenomena such as solubility and diffusivity of gases in polymers, dilation of polymers and in the development of applications such as foams and barrier materials.

In this paper, we describe the interactions of compressed CO₂ with isotactic polypropylene (PP). Crystallization of various PPs in presence of compressed CO₂ was evaluated using a high pressure differential scanning calorimeter (HPDSC). CO₂ plasticized the polymer matrix and decreased the crystallization temperature, T_c by $\sim 8^\circ\text{C}$ for PP at a pressure of 650 psi CO₂. The decrease as a function of pressure was $-0.173^\circ\text{C}/\text{bar}$ and did not change with the molecular architecture of PP. Both crystallization kinetics and melting behavior are evaluated.

Since solubility and diffusivity are important thermodynamic parameters that establish the intrinsic gas transport characteristics in a polymer, solubility of CO₂ in PP was measured using a high-pressure electrobalance and compared with cross-linked polyethylene. At 50 °C, solubility followed Henry's law and at a pressure of 200 psi about 1% CO₂ dissolved in PP. Similar solubility was achieved in PE at a pressure of 160 psi. Higher solubility of CO₂ in PE is attributed to its lower crystallinity and lower T_g , than PP. Diffusion coefficients were calculated from the sorption kinetics using a Fickian transport model. Diffusivity was independent of pressure and PE showed higher diffusivity than PP. Preliminary foaming studies carried out using a batch process indicate that both PP and PE can be foamed from the solid state to form microcellular foams. Cell size and cell density were $\sim 10\ \mu\text{m}$ and $10^8\ \text{cells}/\text{cm}^3$, respectively in PE. Differences in morphology between the foams for these polymers are attributed to the differences in diffusivity.

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1. Introduction

Interaction of polymers with compressed gases or supercritical fluids has been widely studied in the literature [1–6]. It is now well established that supercritical fluids can plasticize polymers, leading to

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depression in the glass transition temperature, T_g , to almost the same extent as influenced by vapors or liquids. Chiou et. al. were the first to recognize that supercritical CO_2 can induce crystallinity in amorphous poly(vinylidene fluoride) [3]. Changes in kinetics and morphology have also been achieved in polymers such as poly(ethylene terephthalate) [3,4], polycarbonates [5], poly(ether ether ketone) [1], etc. In the case of syndiotactic polystyrene, absorption of CO_2 leads to an acceleration of relaxation times that causes a lowering in the glass transition temperature and an increase in crystallization kinetics [2]. This plasticization effect leads to new solid–solid phase transitions. A recent publication [6] indicated that CO_2 can also plasticize polypropylene. Besides supercritical CO_2 , other gases such as methane and ethylene also plasticize polymers, but to a much lesser extent than CO_2 [7].

Supercritical fluids have several advantages over vapors or liquids. The thermodynamic activity of a vapor is limited by its saturation vapor pressure, and that of a liquid by its solubility in the polymer. The activity of a supercritical fluid changes by varying the pressure. Thus, these fluids provide a highly tunable technique to change the morphology or crystallinity in a controlled manner. Furthermore, fluids like CO_2 are easily removed from the polymer matrix by depressurizing the system once the desired morphology is achieved. Interactions of polymer with supercritical CO_2 and associated applications depend on whether the polymer dissolves in the gas or the gas dissolves in the polymer. Solubility and diffusivity of the gas are two critical thermodynamic parameters that establish intrinsic gas transport characteristics. Gas solubility dictates the nucleation of cells and final cell characteristics in foams. Diffusivity of the gas controls the growth of the cells from the polymer matrix and can be obtained from the absorption kinetics [8]. Among the various applications resulting from the interactions of the supercritical gases with polymers, foams is a fast growing industry. The potential for polyolefin foams made with CO_2 is only beginning to be realized [9]. Fundamental knowledge on gas solubility, the impact of crystallization on foam cell nucleation and growth, and the role of polymer morphology in controlling foam structure, etc., are lacking in the literature.

This paper describes the effect of supercritical CO_2 on phase behavior, crystallization kinetics and morphology of polypropylene. Also described in this

paper are the solubility/diffusivity measurements and preliminary foaming studies on polypropylene and cross-linked polyethylene.

2. Experimental

2.1. Sample description

Various PPs used in this study were as follows: iPP-1 (Metallocene linear PP, M_w/M_n 2.1, total defects 1.2/100 monomers); iPP-2 (Ziegler-Natta linear PP, $M_w/M_n \sim 3.5$, MFR 5 (EscoreneTM PP1012)); and iPP-3 (Ziegler-Natta linear PP, MFR 5.6 (ProfaxTM 6501)). The cross-linked polyethylene used for solubility and foamability studies had a glass transition temperature, T_g of -38°C and its crystallinity obtained from heat of fusion was 29%.

2.2. Crystallization and melting in presence of supercritical CO_2

A TA Instruments 2910 high pressure DSC adapted for crystallization studies of polymers at sub-ambient temperature was used. In addition to the crystallization experiments at a constant cooling rate of $10^\circ\text{C}/\text{min}$, it was possible to obtain faster cooling rates ($\sim 20^\circ\text{C}/\text{min}$). Since pressure cells cannot be cooled with a refrigerated coolant, cooling is achieved by blowing house air over the cell. Helium (50 psi) is added to the pressurizing gas to enhance the conductivity of the cell. This enabled us to determine the crystallization kinetics under pressure. The HPDSC can be used up to 1000 psi, from ambient to 300°C . Both hydrostatic pressure and interactions of gases with polymers can be studied.

All measurements were carried out in an encapsulated aluminum pan, with three pin holes in the lid, to allow gas to interact with the polymer. In a typical experiment, about 5 mg of polymer was pressurized with supercritical CO_2 at room temperature (RT). In all experiments, 50 psi helium is added to CO_2 . The polymer was heated to 210°C at $10^\circ\text{C}/\text{min}$ and held for 15 min for the gas to thoroughly mix with the melt. The results from the HPDSC measurements were quite reproducible indicating that samples crystallized from the melt-state had almost complete mixing with the gas. Crystallization measurements were

carried out at a cooling rate of 10 °C/min and pressure of CO₂ ranged from 350 to 830 psi (maximum allowable pressure at the critical temperature of 32 °C). Following crystallization, the polymer was slowly degassed at room temperature to completely remove the dissolved CO₂. The degassed samples were analyzed on heating to evaluate the melting behavior. Experiments were also conducted with poorly soluble helium at various pressures to compare with the samples treated with CO₂.

2.3. Solubility measurements

Solubility of compressed CO₂ in PP and cross-linked PE were carried out at the laboratories of the National Research Council (NRC), Ottawa, Canada, using a gravimetric technique. A specially adapted Cahn D110 ultra-sensitive electrobalance was used. The details of the technique are described in [8]. Briefly, about 1 g of polymer, in the form of 12 mm diameter × 0.25 mm thick disk, was placed on the sample side of the balance and glass beads weighing approximately the same as the polymer were installed on the reference side of the balance. An appropriate amount of nichrome wire was then added to the sample side such that the mass and volume of the two sides were matched as much as possible to minimize the effect of buoyancy. The sample was degassed for 3 days at 50 °C before starting the measurements. At a given pressure, the microbalance simply recorded mass every 10 s, until a constant value was obtained. Once the system attained constant mass, the pressure was increased to the next value and this was continued until the pressure range of 40–200 psi was covered. The pressure was then decreased in small steps, and a constant mass was established at each step to determine the diffusivity of CO₂.

2.4. Foaming of PP and PE

Films of the size of 30 mm × 10 mm × 0.76 mm were saturated with CO₂ at room temperature for 3 h in a pressure vessel. The pressure was gradually released and the saturated films were quickly placed in a pre-heated oil bath for a specified time to foam the sample. The temperature of the oil bath was kept close to the onset of the melt of the polymer so that some amount of pre-melting occurs in the polymer. The foamed

specimens were quenched in tap water to freeze the foamed morphology. In these samples, foaming time and temperature were varied only slightly. Density of the samples was determined by weighing the foamed polymer in water and air, using a balance with a resolution of 10 μg. For microstructural analysis, foamed samples were fractured at liquid nitrogen temperature and analyzed using a JEOL, JSM 5300 scanning electron microscope.

3. Results and discussion

3.1. Effect of CO₂ on crystallization of PP

Fig. 1 shows the crystallization of iPP-1 in presence of supercritical CO₂. At a pressure of 650 psi, CO₂ lowers the crystallization temperature, T_c decreased by about 8 °C. CO₂ also lowered the crystallization of iPP-2 (decrease at 650 psi was about 6 °C). The slightly higher crystallization temperature in iPP-1 is related to its narrow molecular weight distribution and has been described earlier in the literature [10]. Fig. 2 shows the effect of pressure of CO₂ on plasticization of various PPs. At all pressures, a decrease in crystallization temperature was observed for the various PPs. In addition, the decrease was linear with pressure. The slope of the T_c –pressure profiles gives a measure of the solubility of CO₂ in PP (e.g. dT_c/dp for iPP-1 is -0.173 °C/bar). Since both iPP-1 and iPP-2 show a similar decrease in crystallization temperature,

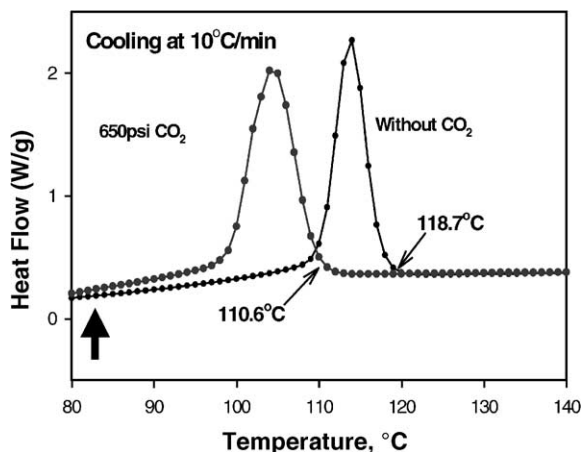


Fig. 1. Crystallization of iPP-1 in presence of compressed CO₂.

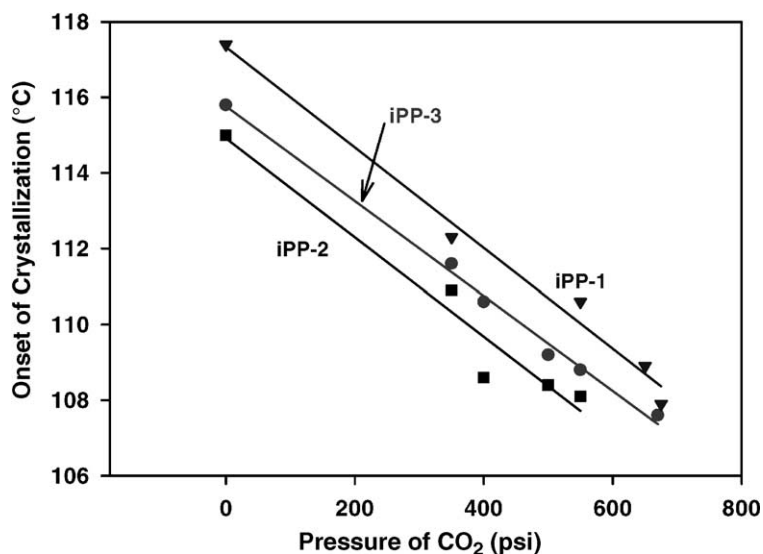


Fig. 2. Plasticization of various PPs by compressed CO₂.

differences in molecular weight distribution and defect content in polypropylene do not appear to influence solubility of CO₂ in PP.

The interactions of the low molecular weight molecules (CO₂) with the polymer decreases the relaxation time of the polymer. The gas absorbs in the amorphous regions of the polymer and dilates the polymer matrix. This leads to a lowering of the energy barrier, so that the phase transitions occur at a lower temperature. Plasticization of polymers with compressed gases has been widely studied in the literature, for example, in polymers like polystyrene [2], etc. Since all iPPs show similar values for the glass transition temperature, they plasticize to the same extent.

3.2. Melting behavior of PP in presence of CO₂

Plasticization of PP with CO₂ can be evaluated from both crystallization and melting analysis. Melting temperature decreased linearly with increase in CO₂ pressure for various PPs heated at 10 °C/min. In the case of iPP-1, T_m (onset) decreased from 147 °C at ambient pressure to about 141 °C at 650 psi. A similar decrease was also observed for iPP-2 (onset of melting decreased from 154 to 148 °C). Earlier measurements carried out under close to equilibrium

conditions (heating rate 2 °C/min) reported a decrease of about 11 °C in the onset of melting [6]. A lower decrease in our measurements suggests that during the melting of the polymer in a conventional DSC, some of the gas may have been desorbed. It appears that a similar amount of desorption occurs in all the experiments carried out on the HPDSC and it is possible to use the melting results to evaluate the plasticization effect of CO₂. The change of T_m versus pressure of CO₂ for various polypropylenes in our measurements results in a slope of -0.124 °C/bar, and agrees well with that reported in [6] (-0.120 °C/bar).

3.3. Melting behavior of PP in absence of CO₂

PP crystallized from the melt in presence of 615 psi CO₂ was evacuated to remove the dissolved CO₂ at room temperature. Melting behavior was analyzed to determine the effect of CO₂ on crystalline phase transitions of PP. The results are shown in Fig. 3a and b for iPP-1 and iPP-2. In Fig. 3a, the slightly lower melting temperature of the monoclinic phase at ~ 154 °C may be either due to the presence of residual CO₂ or due to the smaller lamellar thickness of the crystals. In Fig. 3b, both the CO₂ treated and untreated, iPP-2 melts at ~ 164 °C. The higher melting of iPP-2 is well known in the literature [10]. The results for

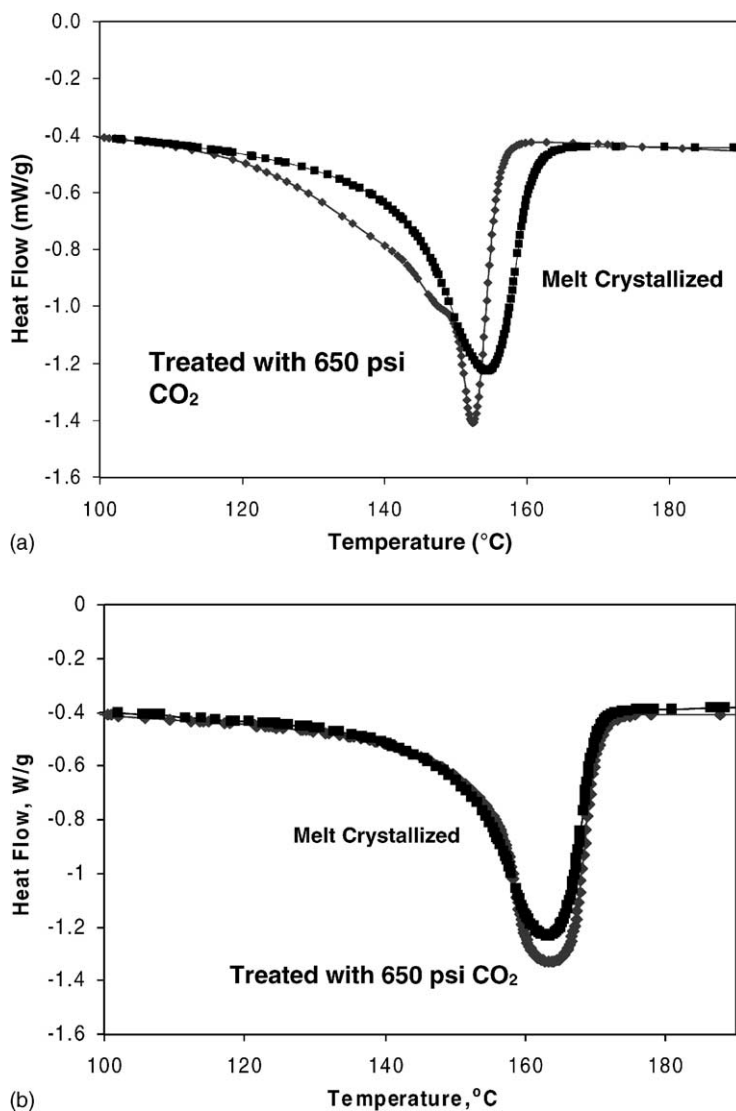


Fig. 3. (a) Melting of iPP-1 crystallized from melt in presence of 650 psi CO₂ and analyzed after degassing CO₂ at RT. (b) Melting iPP-2 crystallized from melt in presence of 650 psi CO₂ and analyzed after degassing CO₂ at RT.

CO₂ treated iPP-2 indicate that interactions with CO₂ do not influence the crystalline morphology. The plasticization effect observed in the presence of CO₂ is essentially due to the effect of the dissolved gas on the relaxations of the amorphous regions of the polymer. Descriptions of the morphology of PP under hydrostatic pressure conditions and at ambient pressure under slow crystallization can be found in references [11,12].

3.4. Crystallization kinetics of PP in presence of CO₂

Fig. 4 shows the isothermal crystallization of the iPP-1 in the presence of CO₂. These data show a decrease in rate of crystallization by addition of CO₂. The half time for 50% crystallization increased from 2.1 min for untreated PP to 2.6, 4.5 and 8.0 min for 100, 220 and 400 psi CO₂. The isotherms display the general features characteristic of polymer crystalliza-

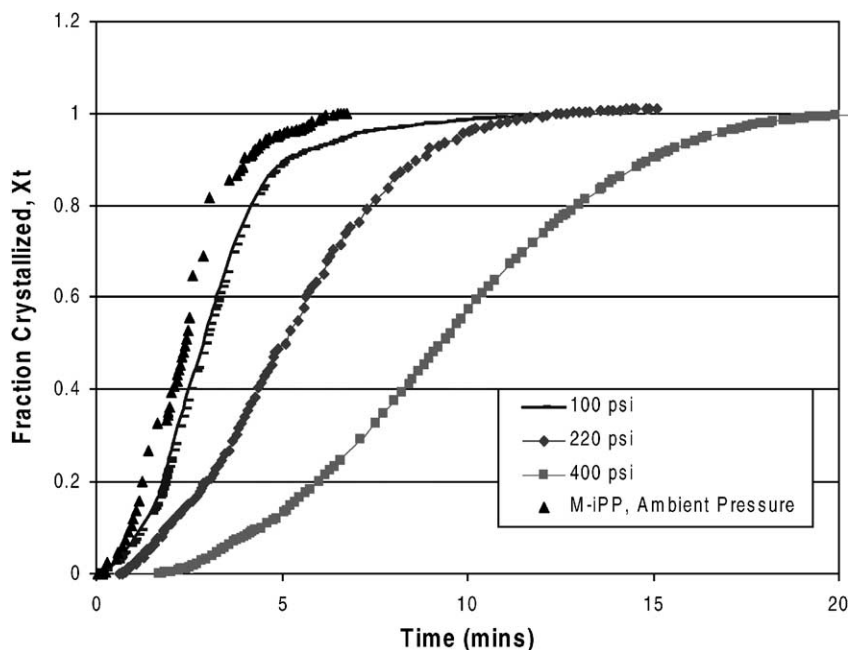


Fig. 4. Crystallization isotherms of iPP-1 at 126 °C under various CO₂ pressures.

tion. The sigmoidal shape of the isotherms is typical of the nucleation and growth crystallization process. In contrast to the crystallization at various temperatures, the isotherms do not superimpose one another. The basic theory of crystallization kinetics as formulated by Avrami [13] and applied to polymers [14] can be used to analyze the data for determining the changes in nucleation and growth processes. The theory takes into account the impingement of growing centers but has several limitations [14]. At small extents of transformation, the Avrami equation is written as 1 and the double log form is written as Eq. (2).

$$1 - X(t) = Kt^n \quad (1)$$

$$\log[-\ln(1 - X_t)] = n \log(t - t_i) + \log K \quad (2)$$

where X_t is the extent of crystallinity induced at a time t , t_i the induction time for nucleation, n the Avrami exponent and K is the kinetic rate constant for nucleation and growth. Though the Avrami model has several limitations, it can be used to give an approximate analysis of the crystallization mechanism.

Avrami plots for iPP-1 are shown in Fig. 5. For PP crystallized without CO₂, the value of ' n ' was 2.1.

Values reported in the literature range between 2 and 3 and indicate a spherulitic growth pattern [14] typical of polymer crystals. On treatment with CO₂, ' n ' decreased slightly (overall ' n ' is ~ 1.7 for all pressures). In addition, a slight change in slope occurs at all pressures. These results indicate a change in crystallization mechanism (nucleation or crystal growth stage) upon treatment of PP with CO₂. Thermodynamic melting temperature does not change upon treatment with CO₂. The supercooling ($\Delta T = T_m - T_c$) increased from 30 °C for untreated to 39 °C for PP treated with 650 psi CO₂, as the energy barrier to nucleation increased due to interactions with the gas. In addition, formation of a lower melting crystal phase, may also contribute to changes in crystal growth and thus ' n ' for iPP-1.

3.5. Solubility and diffusivity of CO₂ in PP

An ultra-sensitive microbalance was used to determine the solubility of CO₂ in PP. The solubility data obtained at various pressures at 50 °C are plotted in Fig. 6. Analysis of solubility data using the approach described in [15] indicates that solubility

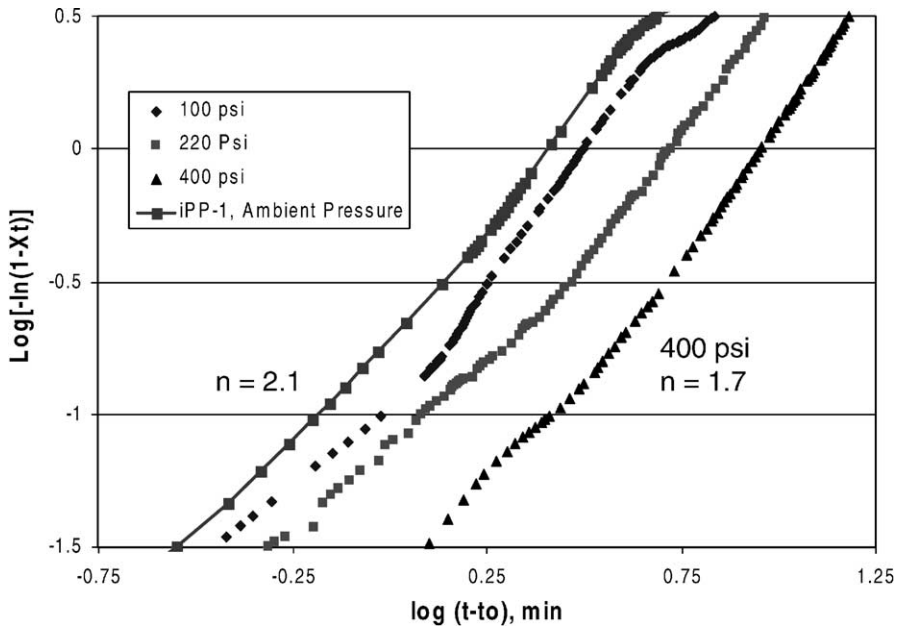


Fig. 5. Avrami Plots for iPP-1 at 126°C under various CO₂ pressures.

follows Henry’s law. About 1% CO₂ can be dissolved in PP at this temperature at 180 psi. The slightly higher solubility in polyethylene is due to its lower glass transition than PP. Almost similar solubility in these polymers suggests similar characteristics in

foam process, gas separation membranes and barrier materials.

The diffusion coefficients were calculated from sorption kinetics using a Fickian transport model as described in [15]. The data are plotted in Fig. 7.

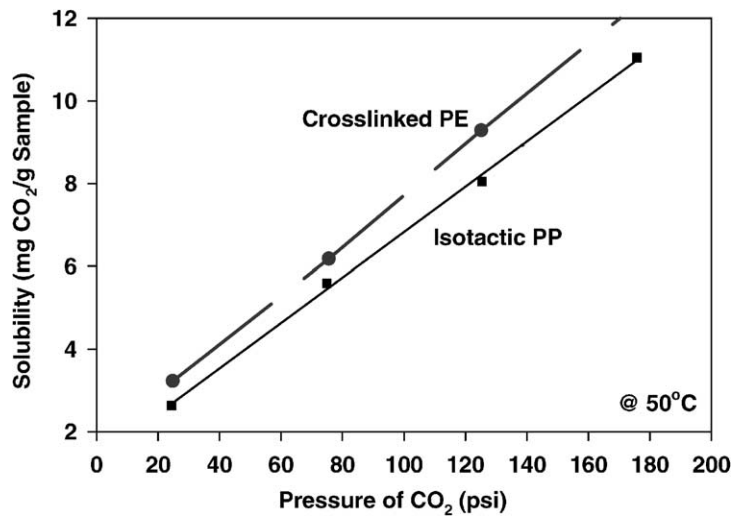


Fig. 6. Solubility of CO₂ measured on a high pressure microbalance.

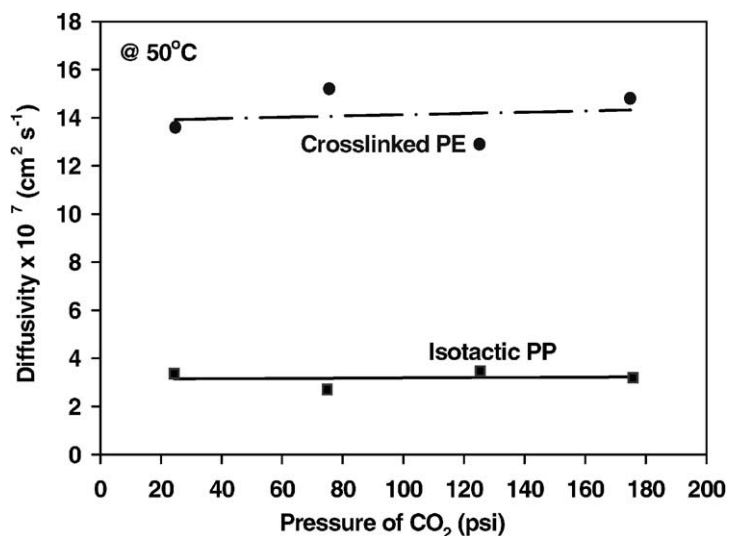


Fig. 7. Diffusivity of CO₂ obtained from the solubility data.

Pressure has no effect on diffusion coefficients since amorphous regions are in the rubbery state. Differences in diffusivity between PP and PE impact morphology of the foam made from these polymers using CO₂ as a blowing agent.

Initial foaming studies using the batch process are shown in Figs. 8 and 9. The polymers were saturated with 800 psi CO₂ at room temperature and then foamed at 150 °C (Fig. 8) and 113 °C (Fig. 9). In both

polymers, closed cell foam morphology can be obtained. The cell size for the larger cells was around 10 μm and cell density was about 10⁸ cells/cm³ in PE (Fig. 8). The results indicate the feasibility of a batch process to develop microcellular foam morphology for polyolefins. The foam cells appear to be well formed in PE while the PP sample (Fig. 8) shows a clear distinction between the skin and core of the injection molded bar. In addition, in the PP foams some

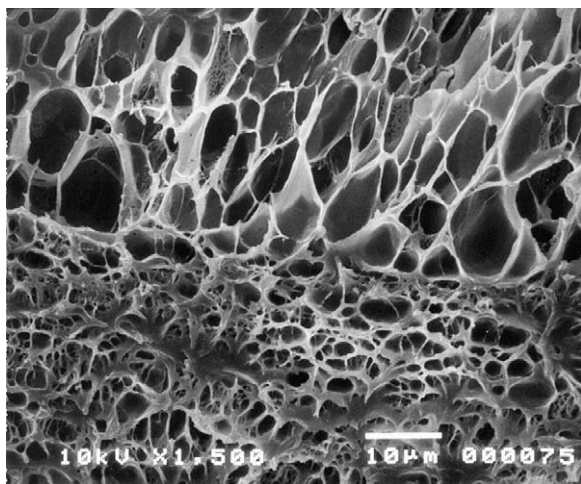


Fig. 8. SEM of CO₂ blown foam from iPP-1.

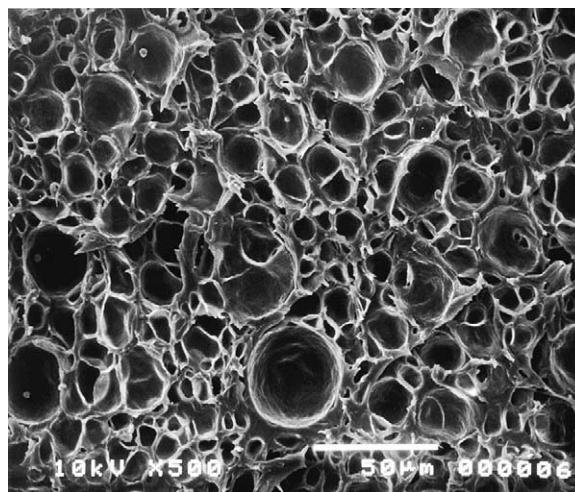


Fig. 9. SEM of CO₂ blown foam from cross-linked PE.

of the cells appear to be ruptured. The differences in morphology between PP and PE are due to the differences in solubility and diffusivity of CO₂. Formation of ruptured cells in PP indicates that the foaming temperature was close to the melting temperature and the melt strength was therefore not high enough. Presence of cross-links in PE probably contribute to the better dimensional stability of PE foams than linear PP. Further, foam density and cell dimensions are also dependent on the foaming temperature and time of foaming. These need to be more carefully evaluated.

4. Conclusions

Work is ongoing to conduct a comprehensive study on the crystallization behavior of polypropylene using supercritical CO₂. Crystallization behavior dictates the morphology and resultant physical properties. If changes in kinetics and morphology can be obtained and fine tuned with the choice of compressed gas, this may show the way to unique properties and also direct the way to new applications, such as micro-cellular foams where PP is today not the polymer of choice.

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