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Autoclave Foaming of Poly(ϵ -Caprolactone) Using Carbon Dioxide: Impact of Crystallization on Cell Structure

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Abstract

The purpose of this study was to develop a better understanding of the main mechanisms controlling the foaming of poly(ϵ -caprolactone) (PCL), a semi-crystalline biodegradable polymer, using batch processing and CO₂ as the physical blowing agent. A detailed study of the dissolution of CO₂ was conducted in order to establish its impact on the transition temperatures of PCL. In a following step, particular attention was paid to the effects of crystallization on cell structure. This foam structure was subsequently linked to the processing window, expressed in terms of the processing temperature with respect to the shifted crystallization temperature and modified crystallization kinetics of PCL. The effects of talc addition on PCL crystallization and foam structure were also investigated, as talc is expected to modify the nucleation rate of crystallites and cells.

1. Introduction

The vast majority of commercial polymeric foams deals mainly with polystyrene (PS), high-density and low-density polyethylene (HDPE, LDPE), polypropylene (PP), polyvinyl chloride (PVC) and, to a more limited extent, polyethylene terephthalate (PET). Interests in the extrusion-foaming of biodegradable polymers such as polylactic acid (PLA), poly(ϵ -caprolactone) (PCL) and thermoplastic starch [1] have been recently expressed. Such studies are very relevant since the manufacturing of biodegradable foams is a challenging step in the development of completely biodegradable/compostable packaging systems. At the same time, due to intense political and environmental pressures, the production of ozone-damaging physical blowing agents such as chlorofluorocarbons (CFC) has been prohibited, while that of hydrochlorofluorocarbons (HCFC) is currently undergoing a phasing out. Thus, new environmentally-friendly

alternative blowing agents such as carbon dioxide and nitrogen are being considered for foam applications.

Two methods for manufacturing thermoplastic foams are commonly reported, i.e. continuous extrusion foaming and batch processing. In the first case, the physical blowing agent is fed up with the polymer melt at elevated temperatures and pressures into the extruder. Then the polymer/gas melt is subsequently foamed beyond the die of the extruder. In contrast to high glass transition temperature (T_g) amorphous polymers, the extrusion foaming of semi-crystalline polymer such as PP is known to be very difficult and restricted to a very narrow temperature range. This is due to the linearity of the chain structure that is associated with the lack of “strain hardening” usually observed for branched structure, as typically encountered in LDPE for instance. Constant [2] showed that the desirable foam processing window seen with LDPE is provided from the long chain branching (strain hardening) and, to a lesser extent, from a “more desirable” crystallization behavior. They claimed that slow crystallization rate at a process temperature approaching the crystallization temperature (T_c) seems optimum for making high quality, low-density foam. Obviously, the crystallization kinetics appears to be a relevant factor in the foam processability.

The batch processing, also called the autoclave method, is associated mainly to small production of microcellular foams, although large-scale commercial production has also been reported [3]. In this two-stage batch process, the polymer sample is placed in a high-pressure gas environment, resulting in the diffusion of gas into the polymer matrix. Nucleation and bubble growth are induced following two different paths, either through a controlled depressurization in the autoclave (called the pressure-quench method) or from the temperature rise induced in a hot fluid bath (temperature soak process). Even if the physical mechanisms behind these two foaming methods, extrusion and autoclave, are very close, the dynamic is completely different and the batch process generally allows the control of foaming over the largest possible temperature range.

Over the last two decades, the research on batch polymer processing has mainly focused on the foaming of amorphous polymers, such as PS, polycarbonate (PC) and poly(methyl methacrylate) (PMMA). However, very little work has been done on the foaming of semi-crystalline polymers. Baldwin *et al.* [4] have demonstrated for PET/CO₂

system that crystallinity plays a major role in microcellular processing through its effects on both cell nucleation mechanisms and cell growth. Since the gas does not dissolve in the crystals, the polymer gas mixture formed during the microcellular processing was not uniform. As a result, the bubble nucleation was also non-homogeneous throughout the sample due to the heterogeneous nature of the semi-crystalline polymer matrix. Furthermore, crystallinity severely increases the matrix stiffness of the semi-crystalline matrix compared to its amorphous counterpart, which limits or inhibits severely the cell growth. To partially circumvent these problems, Colton [5] produced microcellular structures of semi-crystalline PP using a high temperature processing technique, i.e. above the melting point. The polymers were thus processed in the molten, amorphous state. However, according to several authors, [4, 6], it seems that small crystalline content and small crystal nuclei density resulted in foams with a much more uniform and finer cellular structure than samples having a high level of crystallinity and a low crystal nucleation density.

Another issue in the foaming process of semi-crystalline polymer is the effect of the dissolution of gas molecules into the polymer. It is now well known for amorphous polymers that this phenomenon causes significant plasticization, resulting in decreasing significantly the T_g . Therefore, depletion of the gas from the gas-swollen melt can induce a rapid viscosity increase if the processing temperature is close to the glass temperature of the neat amorphous polymer. Obviously, the polymer/gas solution formation process is much more complex with semi-crystalline polymers compared to amorphous resins. In fact, with the increase of the free volume of the polymer by the dissolved molecules (swell), the chain mobility is enhanced, thereby the crystallization onset is modified as well as its kinetics. Crystallization of amorphous PET induced by sorbed CO₂ has been investigated by several authors [4, 7, 8]. The major finding of their works was that PET crystallizes at a lower temperature in the presence of high CO₂ solution concentrations. Similar depression in the crystallization temperature has been reported by Schultze *et al.* [9] for poly(p-phenylene sulphide) in presence of carbon dioxide. This effect can be advantageously used in specific cases. For instance, the introduction of CO₂ molecules into syndiotactic-polystyrene (sPS) induces the transition between various crystalline forms (i.e. solid-solid transition) that could not be produced by other methods [10].

Another interesting example is given by the work of Handa *et al.* [11]. They observed that tert-butyl poly(ether ether ketone) (tBuPEEK) crystallizes readily when annealed in the presence of compressed CO₂ whereas it does not crystallize at any temperature between its T_g and the dissociation/degradation temperature while annealed in the absence of dissolved gas. However, that induced-crystallization is often a disadvantage for the production of microcellular foam because the cellular structure of semi-crystalline polymer foams is relatively difficult to control compared to that of amorphous polymer foam.

The purpose of this study was to develop a better understanding of the main mechanisms controlling the foaming of PCL using batch processing and CO₂ as the physical blowing agent. PCL is a semi-crystalline biodegradable polymer, with a repeating molecular structure that consists of five non-polar methylene groups and a single relatively polar ester group. Therefore, unlike aromatic polyester such as PET that contains stiff backbone chains, thermal crystallization of PCL is relatively quick and even occurs at room temperature. A detailed study of the dissolution of CO₂ in PCL was conducted, focusing mostly on its impact on the transition temperatures of PCL. The batch foaming of PCL using a physical blowing agent such as CO₂, N₂ or a mixed of the two has already been explored by several authors [12, 13, 14]. However, these foaming experiments were conducted at temperatures above the crystallization temperature and thus very little attention was paid to the effect of crystallinity on cell morphology. Therefore, in our study, particular emphasis was paid to the effects of crystallization on the foam structure since the crystallization kinetics and crystallization temperature have been reported to be relevant factors for the foam processability of semi-crystalline polymers. The foam structure was subsequently linked to the processing window expressed in terms of the processing temperature with respect to the shifted crystallization temperature of PCL. The effects of crystallization on the foam structure were also investigated in presence of talc, this latter intended to modify the nucleation of both crystallites and cells. Preliminary results of this work have been already presented at the *Foams 2004 - 4th International Conference on Thermoplastic Foam* [15].

2. Experimental

2.1. Materials

The PCL used in this study was supplied by Dow Chemicals (Tone P787), and a selection of physical properties is reported in Table 1 [16]. The talc used as nucleated agent for selected formulations was manufactured by Luzenac Corporation (Mistron Vapor, mean particle diameter of 2 μm). Commercial-grade carbon dioxide was used as physical blowing agent without any further purification. Since hydrolytic degradation can occur during processing, the polymer was dried prior to processing.

Four different talc concentrations were studied during the course of this investigation (0.5, 1, 2 and 5 wt.%). The PCL and talc were first compounded using a twin-screw extruder, and the resulting pellets were compressed in the shape of approximately 1mm thick sheet using a Carver Press heated at 100°C and then slowly cooled down to room temperature. The sheet was then cut into square samples of 2 cm^2 for absorption and foaming experiments.

2.2. Absorption Experiments

The equilibrium solubility and kinetics for absorption and desorption of CO_2 in PCL at a given set of processing conditions (24°C, 4.82 MPa) were measured according to the gravimetric method described by Berens and Huvard [17]. Sheets of polymer samples were compression-molded at typical thickness of 1.0-1.1 mm, cleaned, weighted and then placed into the pressure vessel subsequently charged with CO_2 up to a constant saturation pressure of 4.82 MPa. The samples were maintained at room-temperature during saturation (i.e. approximately constant at 24°C). Once the desired saturation time was reached, the pressure vessel was quickly discharged in approximately 15 s. The sample was then removed and weighted as quickly as possible, i.e. typically within the following minute. Sample weighing during desorption was done at regular time intervals. The CO_2 mass uptakes were then calculated and the results plotted versus the square root of desorption time. This yielded a linear plot for data reported at short time indicative of Fickian diffusion kinetics. Linear extrapolation to zero desorption time gives the uptake

of CO₂ dissolved at the end of the sorption period. This procedure was repeated for various sorption periods, as reported in Figure 1.

2.3. Normal and High Pressure DSC

The Differential Scanning Calorimetry (DSC) experiments were carried out in a TA Instruments, model Q1000, modified for use under elevated pressure conditions (Q Series Pressure Cell). Once the sample and the reference pans were loaded, the system was pressurized with the gaseous CO₂ at the desired pressure value. The sample was held at constant temperature (usually 26°C for 18 hours) and at the selected CO₂ pressure (varying from 1.03 to 4.83 MPa) to ensure that equilibrium solubility was reached. While still in contact with the gas, the sample was then scanned at 5°C/min, from room temperature to 100°C, annealed 3 min at 100°C and was then allowed to freely cool down to ambient temperature, typically 26°C (see Figure 2 for the as-measured experimental cooling rate). It is worth noting that the pressure in the system did not remain constant during the temperature scan since the high pressure cell was not connected to the CO₂ gas reservoir.

Results on the influence of talc content on crystallization temperature were obtained in a standard DSC cell under N₂ flux. The heating and cooling rates used for all the runs were 2°C/min. The temperature ranged between 0 and 100°C. Peak areas and the resulting heat of transition, as well as the transition temperatures, were analyzed using the TA Analysis Data System.

2.4. Foaming Experiments

The batch foaming experiments were carried out at a set temperature achieved either by heating the polymer/gas solution from the semi-crystalline state or by cooling down the polymer/gas solution from the melt. In the first case, the PCL/talc samples were placed in a pressure vessel and saturated with CO₂ at a saturation pressure of 4.83 MPa for 3 hours at room temperature (this time period being referred as the saturation time). The autoclave was subsequently heated to the selected foaming temperature. In the second series of experiment, PCL/talc samples were saturated for 3 hours at 70°C and a pressure of approximately 6.21 MPa. This pressure strictly corresponds to the increase

pressure due to heating the pressure vessel, initially pressurized at 4.83 MPa, from 24 to 70°C. Then the temperature was freely cooled down (see Figure 2 for the as-measured cooling rate) to the chosen foaming temperature. In both cases, once the foaming temperature was reached, the pressure was released to atmospheric pressure in about 45 s. It is worth noting that the experimental CO₂ gas pressure was slightly different for each foaming temperature: pressures vary roughly between 5.0 and 5.86 MPa for foaming temperatures ranging between 30 and 55°C respectively. However, in first approximation, the pressure is considered as constant over the foaming range investigated.

2.5. Characterization of Foams

Since the glass transition temperature of neat PCL is approximately –60°C, the foamed samples were fractured under liquid nitrogen to preserve the morphological features of the cells. Characterization of the foam samples was accomplished using a Hitachi Scanning Electron Microscope (SEM). Image analysis was performed on the SEM micrographs to quantify foam morphology. Several sampling areas providing more than 150 cell diameters were considered for each given foam sample, such as to provide an unbiased estimate of the volume average diameter. Since the fracture does not cross the cells at their widest point, a correction was applied in order to obtain the true diameter and also to account for polydispersity effect [18]. The typical error for the measurement of d_v is approximately $\pm 10\%$. The SEM micrographs were also used to determine the cell population density, defined as the number of cells per unit volume of the original unfoamed polymer, using the following equation:

$$N_0 = \left(\frac{n_b}{A} \right)^{\frac{3}{2}} \times \frac{\rho_p}{\rho_f} \quad (1)$$

where N_0 is the cell population density (g/cm^3), n_b the number of cells on the micrograph, A the area of the micrograph (cm^2), ρ_p and ρ_f the densities of the unfoamed and foamed polymers respectively.

2.6. Rheological Analysis

Rheological characterization of the different PCL/talc blends was carried out using a Rheometric Scientific constant deformation rheometer (ARES model). The experiments were performed in parallel-plate geometry under a nitrogen atmosphere. Temperature sweep experiments were performed to study the influence of talc content on the severe change in the storage modulus of PCL upon crystallization during cooling. For that purpose, the sample was annealed for 10 min at 100°C to ensure that the polymer was completely molten. Then, the temperature was slowly cool down at a rate of 2°C/min. A dynamic mode with a frequency of 0.1 Hz was used. The deformation was maintained at 2% during all the experiments. It is obvious that the absolute value of storage modulus should be considered as a crude estimate since the disc samples were shrinking during cooling. Moreover, it should be noticed that the experiment was limited to a few degrees beyond the onset of crystallization because of the resulting high matrix stiffness.

3. Results and Discussion

3.1. Absorption

It is critical to know the extent of CO₂ molecules dissolution in the polymer matrix. The dissolved foaming agent concentration largely controls the foam expansion process, including the final foam density and cell morphology. Unfortunately, literature is very scarce on the solubility and diffusivity of CO₂ in PCL. Since no data was available at the time this study was conducted, sorption tests were undertaken to provide such information. A series of sorption experiments were consequently performed to evaluate the time required to reach equilibrium conditions. Figure 1 shows a representative 24-h plot for absorption of CO₂ by PCL. Approximately 13% CO₂ can be dissolved in the PCL sample within 2-3 hours. Further increase of the sorption time up to 24-h did not show any change in this equilibrium mass uptake. Based on these results, all sorption times associated to foaming experiments for temperature at or above 24°C were taken at a minimum of 3h to ensure maximum CO₂ uptake and that uniform gas concentration was obtained throughout the sample. Presumably, absorption experiments carried out at temperatures higher than 24°C will reach equilibrium much more rapidly.

Since gas molecules only dissolve through and in the amorphous phase of the polymer, the measured solubility of CO₂ in PCL should be corrected with respect to the volume fraction of amorphous phase which gives a huge 26 wt.% of dissolved CO₂ at a crystalline content of 50% (see the next section for more details). This high solubility of CO₂ molecules in PCL may be explained by the affinity, most probably of weak Lewis acid-base nature, between the carbonyl group (C=O) and the CO₂ molecules, as demonstrated in several studies based on PMMA [19, 20]. Indeed, the gas sorption is not a purely physical phenomenon, but it rather strongly depends on specific chemical interactions between the dissolved molecules and the polymer. Researches conducted in the 1990s on the use of supercritical carbon dioxide as a process solvent have demonstrated that the solubility of polyethers in CO₂ can be drastically increased by addition of either acetate groups in the side-chain or carbonate groups in the backbone of the polymer [21].

The diffusion coefficient D of CO₂ into PCL was calculated using the equation derived by Crank [22] for diffusion in a plane sheet, based from the time required for half of the CO₂ to be absorbed by the polymer:

$$D = \frac{0.049l^2}{t_{1/2}} \quad (2)$$

where $t_{1/2}$ is the half time of the sorption process and l is the plane sheet thickness. This equation implies nevertheless the following assumptions: (i) one-dimensional diffusion is assumed since the thickness of the samples is much smaller than the other dimensions, (ii) the diffusion coefficient is constant and (iii) the sheet does not swell, i.e. the thickness remains constant over time.

Using the above equation, the apparent diffusivity of the PCL system was found to be $5.2 \times 10^{-7} \text{ cm}^2/\text{s}$ for the semi-crystalline PCL sample. Comparing aromatic polyester to aliphatic polyester, one should note that this diffusion coefficient with PCL is much higher than that reported by Baldwin *et al.* [4] for PET, i.e. $8 \times 10^{-9} \text{ cm}^2/\text{s}$ (saturation conditions: 20°C and 5.51 MPa). Considering the much stiffer nature of PET chains ($T_g \sim 75^\circ\text{C}$) as compared to the mobile PCL molecules ($T_g = -60^\circ\text{C}$), the large difference in D observed is plausible.

3.2. Effect of CO₂ on Crystallization

As mentioned in the introduction part, one of the key-issues in the production of cellular semi-crystalline polymers is the crystallization and the resulting change in viscoelastic behavior. Therefore, it is of critical interest to evaluate if the CO₂ dissolution impacts the crystallization of PCL in the solid state. Thus, to further verify that CO₂ did not modify the crystallization of PCL in the solid state, the samples were thermally analyzed before and after saturation. The levels of crystallinity reported on Figure 1 were measured after a one-month desorption period, which was found to be sufficiently long to allow complete removal of the carbon dioxide from the sheets. The indicated degrees of crystallization are based on a mass fraction relative to a maximum PCL heat of fusion of 139.5 J/g as reported by Crescenzi *et al.* [23]. As showed in Figure 1, the constancy of this value at about 50% clearly indicates that there is no change in the crystallinity of PCL samples over the saturation period investigated, as compared to the virgin sample. It is important to note, however, that the sheets used for performing the experiments were initially exhibiting levels of crystallinity close to the maximum achievable with PCL. The compression molding method used for manufacturing the sheets was naturally leading to very crystalline samples. Similar experiments made on less crystalline PCL samples may lead to much different observations.

Baldwin *et al.* [4] demonstrated that the crystallinity of PET increased from less than 5% (initial sample considered as amorphous) to about 30% in the presence of high CO₂ concentrations (saturation pressure: 5.52 MPa; sorption time: 25-h; saturation temperature: 20°C). In their work, they reported a characteristic knee in the transient gas mass uptake curve, indicative of CO₂ rejection accompanying the induced PET-CO₂ crystallization. As the solubility of gas in polymer is approximately a linear function of crystallinity (no gas is allowed to dissolve in the crystalline phase), increasing crystalline fraction decreases the global system solubility (in first approximation, the equilibrium solubility of the amorphous phase can be considered as a constant). However, in our case, no distinctive knee in the mass uptake curve was observed. Rather, an exponential increase with a plateau value was obtained which could be interpreted as if no additional crystallization occurred compared to the neat PCL sample, thus reinforcing the conclusions drawn from the DSC measurements.

Figure 3 shows the *in-situ* high pressure DSC heating cycles of the PCL-CO₂ system at various CO₂ pressures. For neat PCL, a melting temperature T_m near 60°C and a crystallization temperature T_c of approximately 37°C were observed. The fusion event moves to lower temperatures and becomes broader with an increasing CO₂ pressure, as clearly displayed in Figure 3. For instance, it decreases down to nearly 46°C (at peak maximum) for a CO₂ saturation pressure of 4.83 MPa, i.e., for a gas concentration of roughly 13 wt.%. Similarly, the PCL crystallization peak observed at a CO₂ saturation pressure of 1.03 MPa is decreased by ~5°C, as shown in Figure 3b and Table 2. Unfortunately, equipment-related limitations prevents T_c observation for CO₂ saturation pressure larger than 1.03 MPa, the minimum temperature achievable during the cooling cycle of the high pressure cell being *ca.* 30°C. However, one would expect that the crystallization peak shifts continuously to lower temperatures with increasing CO₂ saturation pressures.

The variations in T_m and T_c for PCL-CO₂ are plotted against the CO₂ pressure p in Figure 4. T_m - p curve is linear with a negative slope of roughly -2.9°C/MPa. Similar behaviors have been observed for other semi-crystalline polymers pressurized with CO₂, such as PET and sPS [24]. Their respective T_m depressions with pressure were -0.725°C/MPa and -2.32°C/MPa, this last value for sPS being close to that found for PCL.

It is rather difficult to conclude about the depression in crystallization temperature of PCL due to CO₂ dissolution. Nonetheless, the crystallization temperature at a saturation pressure of 2.07 MPa can be estimated from the onset crystallization peak, assuming that peak width was not modified while increasing CO₂ saturation pressure from 1.03 to 2.07 MPa. In that case, it is thus possible to extrapolate to higher CO₂ pressure the T_c values observed at low CO₂ saturation pressure, as shown in Figure 4. It was found that the maximum crystallization rate of neat PCL should occur near 16°C for a saturation pressure of 4.83 MPa. However, as the crystallization peak was not experimentally observed for pressures higher than 1.03 MPa, the above-extrapolated effect for high CO₂ saturation pressure must be taken with caution for further discussion on the foam analysis. In fact, the data presented here are intended to be used for explaining the cellular morphology presented in the following sections. The T_c depression with pressure for PCL is thus approximated as -2.9°C/MPa, and similar results have been reported by

Shultze *et al.* [9] for poly(p-phenylene sulfide)-CO₂ system (cold crystallization; -2.17°C/MPa). In the same way, Handa *et al.* [10] showed for sPS that the dissolved CO₂ lowers the cold crystallization temperatures at a much faster rate of -5.65°C/MPa.

Conceptually, the mechanisms governing the crystallization and the melting events are both related to the chain mobility of the amorphous phase surrounding the crystallites. Thus, it seems reasonable to consider that the crystallization temperature will also decrease linearly with the increase of CO₂ pressure, as long as the anti-plasticization effect caused by the hydrostatic pressure remains small enough, which seems to be the case from the linear decrease of T_m up to 4.83 MPa.

3.3. Effect of Talc on Crystallization Temperatures

It is well known that heterogeneous nucleation allows a better control of cell nucleation process. This is done in many cases using mineral nucleating agent, such as talc [25]. However, their introduction in polymer formulations could also affect the crystallization behavior of semi-crystalline polymers. To investigate this issue, the crystallization behavior of PCL in the presence of talc was examined using classical differential scanning calorimetry. Figure 5 displays the crystallization exotherms of PCL for different talc concentrations, when cooled from the melt state at a controlled cooling rate of 2°C/min. Without talc, the onset of crystallization is close to 40°C and the peak maximum is located around 32°C. However, the addition of only 0.5% talc shifts the melt crystallization peak from 32°C up to ~39.5°C ($\Delta T_c \cong 7.5^\circ\text{C}$ at peak maximum). Further increase in the amount of talc up to 5% also increased the crystallization temperature by an additional 1.6°C. As shown in Figure 5, talc addition also significantly sharpen the crystallization peak, while the normalized enthalpy associated with the crystallization peak is almost constant at 60 J/g. These results clearly demonstrate that talc particles not only nucleate PCL crystal formation, but they also speed up the crystallization kinetics through a volume effect.

Crystallization temperature was also studied using the high pressure DSC with respect to the presence of talc (1 wt.%) and dissolved CO₂ (saturation pressure: 1.03 MPa). Corresponding results are given in Table 2. As expected, the crystallization temperatures of both samples (with or without talc) are shifted to lower temperatures in the presence of

CO₂ dissolution. More interestingly, the shift in crystallization temperature due to talc addition is independent of the presence of the dissolved CO₂, with a constant value of $\Delta T_c \cong 4.5^\circ\text{C}$. In other words, the plasticizing effect of CO₂ only depends on the saturation pressure, irrespective of the talc content in the PCL sample. Presumably, the depression of crystallization temperature for higher CO₂ pressures (i.e. higher CO₂ concentration) is expected to follow the same trend. However, it is worth noting that the crystallization temperature depression due to talc addition is cooling rate-dependent: the faster the cooling rate, the larger the shift in T_c .

3.4. Influence of Foaming Temperature on Foam Morphology

Preliminary experiments have been performed to study the foaming of PCL/talc samples processed at different temperatures between 25 and 70°C from the solid state, with a crystalline fraction of 50%. In practice, the PCL/talc samples were saturated at 4.83 MPa for 3 hours at room temperature (25°C) and the temperature was subsequently increased to the desired foaming temperature. Unfortunately, using that procedure, the PCL/talc had almost no processing window in terms of foaming capability. Typically, below the melting point of the PCL/CO₂ solution (i.e. about 46°C as determined from Figure 3), it appears that the stiffness of the semi-crystalline system was large enough to inhibit cell expansion. Above the melting point of the PCL/CO₂ solution, the melt strength was not strong enough to prevent cell coalescence and/or foam collapsing. Thus the resulting foam structures were unacceptable in all cases, irrespective of the chosen foaming temperature.

The next series of experiments were prepared by saturating molten PCL in the pressure vessel. The gas-saturated melt was then cooled down below the melting temperature of the neat PCL (without CO₂). The depth of the temperature quench explored was limited to cases leading to acceptable cellular structure. The processing temperature being close to the crystallization temperature of the neat polymer, the evolving cellular structure is significantly stabilized by PCL crystallization. A series of PCL/talc foams was produced at various temperatures following that procedure. This method was proven to be very successful, as the foam processing window was found to

be quite large for such a linear semi-crystalline polymer, typically between 30 and 55°C, which gives a operating range of at least 25°C.

The cellular morphologies of the 5 wt.% talc/PCL samples obtained in this way, for foaming temperatures ranging from 30 to 55°C, are shown in Figure 6. Above 55°C, the cell structure was too heterogeneous, typical of polymer melt solutions with inadequate rheological characteristics. Between 35 and 55°C, the cellular morphology mostly consists of polygonal cells similar to a honey-comb structure (see Figures 6b to 6d). Furthermore, all of these PCL/talc foams produced exhibit fairly uniform cell sizes. Surprisingly, the cellular morphology resulting from a foaming temperature of 30°C is completely different from the one obtained at 35°C (see Figure 6a vs. Figure 6b, note the different magnifications used on these two micrographs). When foamed at 30°C, the cellular structure consists of very small, irregularly-shaped open cells. Note that the PCL samples showed no detectable cell structure (i.e., at a resolution of 0.5 μm) when foamed at or below 25°C.

Figure 7a shows the effect of foaming temperature on density of the 5 wt.% talc/PCL samples while Figures 7b and 7c depict the average cell sizes and estimated cell population density, respectively. Three typical regions can be distinguished from Figure 7. Starting at the higher temperatures, they are as follows:

Domain I. Decreasing the temperature from 55°C to 35°C has little effect on the foam density. The foam density decreases linearly as the foaming temperature increases, with a slope of approximately $-0.01 \text{ g/cm}^3/\text{°C}$. In that foaming range, the cell population density is almost constant at 10^6 cell/cm^3 , which is comparable with other polymer/ CO_2 system nucleated with talc. However, the cell size increases linearly with the foaming temperature between 35 and 55°C as shown in Figure 7b. The corresponding slope is roughly $6 \mu\text{m}/\text{°C}$. Since the cell population density is independent of the foaming temperature, the increase in cell size with foaming temperature can be attributed to the viscosity decrease of the matrix material, causing a decrease of the resistance to cell growth.

Domain II. Figure 7 shows different foaming behaviors when the foaming temperature is below 35°C. Figure 7a indicates that foam density increases exponentially up to a value of approximately 1.2 g/cm^3 , as the foaming temperature is decreased down to 28°C.

Accompanying this increase in foam density, the cell population density also increases radically to a value of about 6×10^9 cell/cm³, which lies in the range associated with microcellular foams (10^9 and 10^{15} cells/cm³). At the same time, the average cell size drops to a few microns for a foaming temperature of 30°C. All these data seem to indicate that a particular phenomenon is occurring near 30°C. Crystallization comes naturally as the most obvious explanation. As a first approximation, the crystallization temperature of 5wt.% talc/PCL can be estimated from the data obtained from high pressure DSC measurements for neat PCL (T_c : $\cong 16^\circ\text{C}$; P_{sat} : 4.83 MPa) and the temperature gap measured in normal DSC between the neat PCL and the PCL containing 5% talc ($\Delta T \cong 11^\circ\text{C}$). When combining the effects of gas plasticization and talc nucleation, a crystallization temperature of about 27°C would be expected for the 5 wt.% talc/PCL/CO₂ system. Moreover, the real crystallization temperature encountered during the batch foaming process is probably slightly higher since the cooling rate in that case is lower than that used in the high pressure DSC experiments (see Figure 2). Therefore, it is obvious to conclude that crystallization of PCL sample prevent the cells from growing and thus constitutes a limiting value for foam processing of highly crystalline polymer such as PCL. This issue will be investigated in more details in the following sections.

Domain III. Below the lower bound temperature of 28°C, no foam structure can be obtained. The resulting foam density measured at 28°C corresponds to that of the unfoamed PCL. As expected, no information is available about the cell population density and cell size.

At this point, it is worth exploring in more details the mechanisms governing cell nucleation, cell growth and cell size for the data of Figure 7, in particular for the region associated with the sharp transition in cell morphology (domain II).

3.5. Effect of Talc Content on Cellular Morphology

In order to better understand the transition in morphology between Figures 6a and 6b (domain II in Figure 7), the effect of talc content was studied at different foaming temperatures.

As shown in Figure 8, a large dependence of cell size on talc content was observed for a foaming temperature of 45°C. Clearly, the addition of talc particles produces smaller cells and more uniform cell size distribution. This result is not surprising since it is well established that talc is an efficient nucleating agent commonly used to produce fine-cell thermoplastic foams with a high cell density, a small cell size and uniform cell distribution [25]. Attempts to produce PCL foams without talc have resulted in an unacceptable product, the cell size being too large and the cell density too low, making the addition of talc essential in our study.

Figure 9 shows the SEM micrographs corresponding to the PCL/talc/CO₂ foamed at a temperature typical of domain II, i.e. 32°C, still with different talc contents ranging from 0.5 to 5 wt.%. It can be clearly seen in Figures 9c and 9d that PCL samples containing 2 and 5 wt.% talc exhibit a bimodal cell structure with small and large cells inter-dispersed. Furthermore, the larger cells are comparable in size and shape to those observed for the 5wt.% talc/PCL foamed at 35°C (Figure 6b), whereas the smaller cell structure seems similar to that observed at 30°C (Figure 6a). Another important feature of Figure 9 is that the relative proportion of smaller cells versus larger ones decreases with decreasing talc content. This observation will be investigated more thoroughly in a further paragraph.

Bimodal cell distribution is not an unusual feature, since it has already been reported for microcellular batch processing of semi-crystalline polymers such as PVC [26]. In this study, it has been proposed that the larger cells were nucleated by the pressure drop when the sample were taken out of the pressure chamber at room temperature, whereas the smaller cells were nucleated by heating when the samples were dipped into the hot bath. Successive pressure drops have also be used for the production of bimodal cell distribution as reported for microcellular batch processing of PS in reactor [27] and for the extrusion foaming of polycarbonate with n-pentane [28]. However, in the present study, the foaming technique greatly differs from the typical batch microcellular foaming technique since the foaming is induced inside the pressure vessel in a single step. Therefore, the bimodal cellular structure observed in our case can not be attributed to a similar double-stage nucleation.

Impact of the talc content at a foaming temperature of 30°C has been also investigated, and the resulting foam morphologies are displayed in Figure 10. At this foaming

temperature, the presence of talc has little effect on the relative proportion of small and opened *versus* large closed cells. The foam morphology remains in all cases mainly composed of open micro-cells. However, as in the case of Figure 8 where foaming temperature was 45°C, increasing the talc content seems to decrease the cell size with the associated increase in cell density. If we consider in first instance that the increase in talc content leads to the formation of a higher number of smaller crystals, and that crystals may be the preferential bubble initiation sites, this last result is not surprising.

Image analysis was performed using several fields of view for each sample in order to determine the relative fraction of each type of cell. Quantitative information is reported in Figure 11, where the surface fraction of open micro-cells is plotted as a function of talc content. From the data collected with the foams obtained at 32°C, increasing the talc content from 0.5 to 5 wt.% raises the fraction of open micro-cells from approximately 6 to 49%. For comparison, the results obtained for foaming temperatures of 30 and 35°C are also plotted on this graph. It is interesting to note that for any given talc content, the proportion of those open micro-cells increases with a temperature decrease, up to a foaming temperature, typically below 28°C as reported in Figure 7, where no porosity can be obtained because of the high crystalline fraction. The results displayed in Figure 11 may strongly suggest that the mechanism governing the formation of the smaller open cells is crystalline dependent. The effects of crystallinity on cell density and the mechanisms governing microcellular nucleation will be investigated in the following paragraphs. In fact, two main factors may influence the foam structure in such a critical way.

Firstly, it is believed that the increased cell density of the crystalline foams is the result of the increased heterogeneous nucleation contribution, with the crystals acting as nucleating particles. Indeed, several authors proposed that the interface between the crystalline and the amorphous region is the preferential site for microvoid nucleation due to a higher energy region resulting in a lower free energy barrier [4]. Baldwin *et al.* [29] investigated the effect of crystallization on the cell nucleation density of poly(ethylene terephthalate) and demonstrated that semi-crystalline PET ($X_c \approx 28\text{wt}\%$) can exhibit up to 10^7 times higher cell nucleation densities compared to amorphous PET ($X_c < 10\text{wt}\%$). Contributions from heterogeneous nucleation were identified as the key-factor in that

specific case. On the other hand, Handa *et al.* [30] pointed out that classical heterogeneous nucleation cannot be applied in the case of semi-crystalline polymers since the boundaries between amorphous and crystalline phase are not well defined, and even if they are, calculation demonstrated that the crystallized part possesses a lower surface energy than its amorphous counterpart.

Another explanation is to consider the influence of crystallization on the local foaming agent concentration inside the PCL sample. In fact, since it is known that no gas is allowed to dissolve in the crystalline phase, one would expect that CO₂ molecules are expelled from the newly formed crystals during crystallization, leading to a higher concentration of CO₂ around crystals and thus leading to higher cell population density with smaller sizes. However, at this point, there is no way of testifying that hypothesis.

Secondly, we consider the effect of crystallinity on cell size and the mechanism governing cell growth. Baldwin *et al.* [4] demonstrated that the abrupt decrease in cell size in the PET crystalline foams was primarily due to the increased matrix stiffness associated with crystallization. For instance, the storage modulus of crystalline PET/CO₂ system at 50°C is over twice that of the amorphous PET/CO₂ at the same temperature and CO₂ content, as measured by dynamic mechanical analyzer (DMA). As a result, the average cell size decreased from 115 to 7 μm and the cell density increased from 1.1×10^6 to 1.0×10^8 cells/cm³ for the crystalline foams compared to the amorphous ones. Moreover, they also noticed that the amorphous foam had honeycomb structures while the crystalline foams had spherical cells with relatively large inter-bubble distances compared with the average cell size. In our case, it was observed in Figure 7c that the cell size increases almost linearly with foaming temperature from 35 to 55°C, indicating that the cell growth mechanism should be controlled primarily by the viscoelastic properties of the polymer matrix instead of the gas diffusion kinetics. If crystallinity did not affect cell growth mechanisms, one would also expect a fully grown honeycomb structure at a foaming temperature of 30°C. However, neither honeycomb cell nor spread spherical type cells were observed. It is likely that the matrix stiffness, largely controlled by the crystalline content, plays a key role in the smaller open-cells observed in Figure 9 and Figure 10.

To support that hypothesis, the viscoelastic behavior of PCL/talc sample was examined by rheological analysis during cooling from the melt state. Figure 12a shows the storage modulus, G' , of PCL specimens modified with talc concentrations ranging from 0 to 5 wt.%. The temperature sweeps reported were made at a cooling rate of $-2^{\circ}\text{C}/\text{min}$. The addition of talc shifted the onset of the abrupt increase in the storage modulus to a higher temperature ($\Delta T \cong 5^{\circ}\text{C}$) compared to neat PCL. It also produced large increase of the slope of the storage modulus and a 10-fold increase was observed upon addition of 0.5 wt.% talc ($3.6 \times 10^5 \text{ Pa}^{\circ}\text{C}$ vs $4.5 \times 10^6 \text{ Pa}^{\circ}\text{C}$).

To better understand the role of talc content on crystallization, it is helpful to represent the data of the crystallization exotherms (Figure 5) in a different format. The crystallinity level was evaluated as a function of the decreasing temperature by integration of the crystallization peak. From this plot is then possible to trace the evolution of crystallinity as a function of temperature for different talc contents. Corresponding results are presented in Figure 12b. This figure indicates three distinctive behaviors: (i) Above 45°C , all the different PCL/talc formulation are in an amorphous state. (ii) In the region of temperature between 38 and 45°C , it can clearly be seen that for any given temperature, the crystallinity level is a function of the talc content. (iii) However, below 38°C , the crystallinity is almost independent of the talc content for a given temperature. In other words, a narrow temperature range of approximately 7°C exists during cooling, in which the different PCL/talc samples possess different levels of crystallinity at a specific temperature, and this could explain the effect of talc content within a specific temperature range as illustrated in Figure 11. Obviously the absolute temperatures reported in Figure 11 are lower than those identified from Figure 12b, due to the effect of CO_2 that delays the crystallization to lower temperatures as shown in Figure 3 and Table 2.

Finally, if we compare both Figures 12a and 12b, the abrupt increase in G' for each talc concentration corresponds relatively well with the crystallization of PCL/talc sample. All the above results unambiguously demonstrate that for a given range of temperature, the talc content can drastically affect the matrix stiffness by moving the crystallization event to higher temperature, resulting in the different cellular morphologies observed in Figure 9.

4. Conclusions

In this study, the effects of talc content and foaming temperature on cell morphology of PCL foams were investigated using batch processing and CO₂ as the physical blowing agent. From the results, the following conclusions can be drawn:

Through a detailed study of gas sorption into PCL, it was found that CO₂ is highly soluble in PCL with a concentration in the amorphous phase of nearly 26 wt.% ($P_{\text{sat}}=4.83$ MPa and 24°C). In addition, the dissolution of CO₂ was found to have a significant impact on both T_m and T_c , with a negative slope of approximately 2.9°C/MPa for the T_m depression. Induced-crystallization was not observed, possibly due to the high crystalline content already present in specimens at the beginning of the sorption experiments.

Preliminary experiments on the batch foaming of PCL using a simple and direct approach - i.e. saturation at ambient temperature, heating to the selected foaming temperature followed by depressurization – gave very limited expansion and/or poor cellular morphologies. However, a wide and adequate foam processing window ($\Delta T \approx 25^\circ\text{C}$) was achieved by first melting completely the sample, dissolving the gas in the molten state, slowly cooling down to the desired foaming temperature, and finally inducing a pressure quench. Low density foams ($\approx 0.2\text{-}0.4$ g/cm³) with closed-cell cellular morphologies (100-250 μm) were achieved with the addition of talc as nucleating agent.

More interestingly, a very fine and open cell structure (cell diameter in the 10 μm range and cell density in the order of 10^9 cell/cm³) was observed when the foaming temperature was lower than 35°C, which fairly corresponds to the crystal formation in the PCL/CO₂ system investigated. No detectable cell structure was observed when the samples were foamed at/or below 25°C, presumably because of a large crystalline fraction leading to excessive matrix stiffness. However, within that given range of temperature (25-35°C), varying the talc content was found to impact the cell morphology by moving the crystallization event to a higher temperature, thus resulting in various crystalline contents for a given temperature. In particular, the formation of a bimodal cell structure was observed at 32°C where the fraction of micropores, versus large closed-cell structure, increased almost linearly with the talc content. Therefore, it would seem that

the smaller open cell morphology resulted from the higher matrix stiffness due to crystallization, thus limiting the cell growth.

Even though it was unambiguously demonstrated that the formation of smaller open cell structure was crystalline-dependent, the mechanisms that would link the foam morphology, e.g. the cell nucleation and cell opening phenomena, to the formation or presence of crystallites remain unknown. Use of a non-intrusive monitoring technique, such as ultrasound measurement, would undoubtedly contribute to provide clues relative to the PCL crystallization and its impact on cell formation during the desorption of the polymer matrix [31].

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Table Captions

Table 1 : Selected physical properties of PCL Tone P-787 [16].

Table 2 : Effects of CO₂ dissolution and talc content on PCL crystallization, as measured by high pressure DSC. In all cases, the samples were freely cooled down from the melt (100°C) at a cooling rate shown in Figure 2.

Figure Captions

Figure 1: Evolution of CO₂ mass uptake (wt.%) into PCL and crystallinity as a function of sorption time at 24°C and 4.83 MPa. An equilibrium apparent mass uptake of approximately 13 wt.% of CO₂ is reached within 2-3 hours. Note that crystallization is independent of sorption time, with a constant value of *ca.* 50%.

Figure 2: Temperature profiles resulting from different types of cooling used during measurement and conditioning of PCL samples. The autoclave and High Pressure DSC were allowed to freely cool down whereas the normal DSC and rheometer were cooled at a controlled rate of -2°C/min.

Figure 3: *In-situ* DSC traces of semi-crystalline PCL-CO₂ scanned under various CO₂ pressures. (a) Heating mode; (b) cooling mode. Samples were first saturated with CO₂ for 18h under ambient temperature ($T_{\text{sat}}=28^{\circ}\text{C}$) and under the pressure indicated on each curve. After this pretreatment, samples were heated up to 100°C at a rate of 5°C/min, annealed for 5 min at 100°C and then allowed to freely cool down to ambient temperature. The resulting cooling profile is reported in Figure 2.

Figure 4: Variation of the melting and crystallization temperatures (T_m , T_c) of PCL as a function of CO₂ pressure. Value obtained for the crystallization temperature at a saturation pressure of 2.07 MPa (open square) was extrapolated from the onset crystallization peak, assuming that peak width was not modified by increasing the CO₂ saturation pressure from 1.03 to 2.07 MPa. Linear fit on T_m - p curve gives a slope of approximately -2.9°C/MPa. Results reported at no CO₂ pressure correspond to standard DSC runs performed at atmospheric pressure under nitrogen purge.

Figure 5: Influence of talc content on crystallization exotherms of PCL/talc samples cooled from the melt at 2°C/min.

Figure 6: SEM micrographs of 5 wt.% talc/PCL samples processed from the molten state and foamed at selected temperatures: (a) 30°C, (b) 35°C, (c) 45°C, (d) 55°C ($T_{\text{sat}}=70^{\circ}\text{C}$; $P_{\text{sat}}=6.41\text{ MPa}$; $t_{\text{sat}}=3\text{h}$). Caution should be paid to the different scales used in the Figure. See Figure 7 for the corresponding bulk foam density, average cell size and cell density.

Figure 7: Effect of foaming temperature for 5 wt.% talc/PCL on (a) the bulk foam density, (b) the cell size and (c) the cell density. The system was cooled from the melt to the selected foaming temperature after CO_2 gas dissolution ($T_{\text{sat}}=70^{\circ}\text{C}$; $P_{\text{sat}}=6.41\text{ MPa}$; $t_{\text{sat}}=3\text{h}$).

Figure 8: SEM micrographs illustrating the effect of talc content on the cellular structure of PCL foamed at 45°C from the molten state ($T_{\text{sat}}=70^{\circ}\text{C}$; $P_{\text{sat}}=6.41\text{ MPa}$; $t_{\text{sat}}=3\text{h}$): (a) 0.5 wt.%, (b) 1 wt.%, (c) 2 wt.%, (d) 5 wt.% talc. Increasing talc content decreases cell size.

Figure 9: SEM micrographs illustrating the effect of talc content on the cellular structure of PCL foamed at 32°C from the molten state ($T_{\text{sat}}=70^{\circ}\text{C}$; $P_{\text{sat}}=6.41\text{ MPa}$; $t_{\text{sat}}=3\text{h}$): (a) 0.5 wt.%, (b) 1 wt.%, (c) 2 wt.%, (d) 5 wt.%.

Figure 10: SEM micrographs illustrating the effect of talc content on the cellular structure of PCL foamed at 30°C from the molten state ($T_{\text{sat}}=70^{\circ}\text{C}$; $P_{\text{sat}}=6.41\text{ MPa}$; $t_{\text{sat}}=3\text{h}$): (a) 0.5 wt.%, (b) 1 wt.%, (c) 2 wt.%, (d) 5 wt.% talc.

Figure 11: Influence of talc content on the proportion of open micro-cell relative to the cellular structure of PCL foamed at 32°C from the molten state ($T_{\text{sat}}=70^{\circ}\text{C}$; $P_{\text{sat}}=6.41\text{ MPa}$; $t_{\text{sat}}=3\text{h}$) as reported in Figure 9. Are also plotted for comparison the values obtained for foaming temperatures of 30 and 35°C. Zero percent corresponds to a fully large closed-cell morphology whereas 100 percent value indicates a fully small opened-cell structure.

Figure 12: Effect of talc content (wt.%) on (a) storage modulus G' and (b) crystallinity of talc/PCL samples during cooling ($2^{\circ}\text{C}/\text{min}$) from the molten state. The storage modulus was measured at a frequency of 0.1 Hz and the deformation was maintained at 0.2%. The crystallinity was calculated by integration of the crystallization exotherms reported in Figure 5.

Table1

Physical Properties	
Molecular Weight, Number Average (approx.)	80000 g/mol
Melt Flow at 80°C/303 kPa,	0.5 g/10 min
Tensile Strength, 5.08cm/min	41.4 MPa
Tensile Modulus	386 MPa
Elongation at Break (5.08cm/min)	900%
DSC Glass Transition Temp. (T _g)	-69°C
Melting Temperature	60°C
Viscosity at 200°C	150 Pa.s
Density at 23°C	1.145 g/cm ³

Table2

Sample characteristics		T _c (°C)	ΔT _c (°C)
Without CO ₂	Neat PCL	37.1	4.5
	PCL+1% talc	41.6	
With CO ₂	Neat PCL	31.9	4.5
	PCL+1% talc	36.4	

Specimens saturated at 1.03 MPa CO₂ for 18h at 24°C.

Figure 1

Figure 2

Figure 3

(a)

(b)

Figure 4

Figure 5

Figure 6

Figure 7

(a)

(b)

(c)

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

(a)

(b)