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FOAMING BIODEGRADABLE POLYMERS: EFFECT OF DISSOLVED CARBON DIOXIDE ON CRYSTALLIZATION OF POLY(LACTIC ACID) AS PROBED BY ULTRASONIC MEASUREMENTS

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BIOGRAPHICAL NOTES

Jacques Tatibouët obtained his Chemical Engineer's degree in 1971 in Lyon (France). He received his Ph.D. in Material Science in 1987 at the Institut National des Sciences Appliquées de Lyon (France). From 1971 to 1996, he was involved at the same Institute in Materials Science Research and Teaching in the domains of ice physics, polymer physics, composite, non-destructive evaluation and intelligent materials. Since 1996, he has been working as a research officer at the Industrial Materials Institute of the National Research Council of Canada in the field of ultrasonic characterization of polymer and foams.

ABSTRACT

While low-density foam extrusion of amorphous poly(lactic acid) (PLA) has been performed with success, foaming its semi-crystalline counterpart still remains problematic. Blowing agents such as carbon dioxide affect the crystallization kinetics of PLA which has a strong impact on the processing window.

The effect of dissolved CO_2 molecules on the crystallization kinetics of PLA, as well as the decrease of the glass transition temperature, were investigated using an original device that combines ultrasonic and volumetric measurements. Contrarily to high-pressure DSC measurements, applied pressure and CO_2 concentration can be studied independently with this device. Ultrasonic parameters such as sound velocity are very sensitive to crystallization and were thus used to monitor the crystallization kinetics. The crystallization rate was found to tremendously increase with a moderate addition of CO_2 and the results are compared with classical DSC measurements. Impact on foam processing is also finally addressed.

INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable polymer which can be made from renewable resources. It has gained enormous attention in the last decades due to its potential to replace conventional synthetic polymers for packaging applications. Control of the ratio between the two enantiomers, L and D, obtained from the lactide monomer, is of critical importance since it has a large impact on the processing conditions and the end-material properties as well. The presence of at least 7% of D- and *meso*-lactide component enables to generate totally amorphous samples, while PLA with L-lactic acid content greater than 93% are semi-crystalline, with crystallinity up to 40% and variable crystallization kinetics. The glass transition temperature (T_g) of PLA is approximately 59°C, and its melting temperature 169°C. It also exhibits a cold crystallization temperature at roughly 110°C.

PLA can be processed through injection molding, blown molding, sheet extrusion, film forming and even foam extrusion. Extrusion of PLA foams in the 20-30 kg/m^3 density range has been previously achieved, using an amorphous PLA grade (see Figure 1) [1].The PLA was foamed using carbon dioxide, an environmentally friendly physical foaming agent, and the processing temperatures were set typically in the 100°C-range, i.e. roughly 40°C above its T_g. The concentration of CO_2 was found to be a critical parameter, and optimal results were obtained with 7-8wt% of carbon dioxide. Surprisingly, lower CO_2 contents did not lead to significant foam expansion while foams blown at CO_2 contents in the 8-10 wt% range showed severe shrinkage upon ageing. The dimensional stability exhibited by the best low-density foams was correlated to high open-cell contents, thus fast gas exchange with atmosphere.

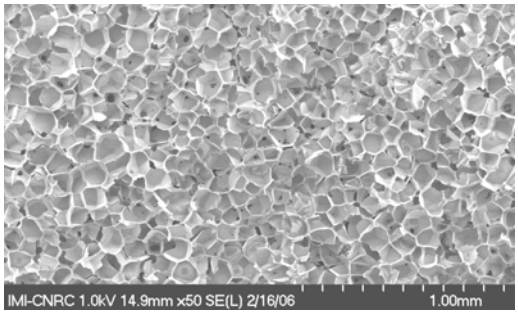

Figure 1. SEM photograph of a PLA foam, with density of 33 kg/m^3, extruded at 100^{o}C using 7.3 wt% of CO_2 and 0.5 wt% of talc.

In order to improve the mechanical properties of the foams, the logical following step was to attempt foam extrusion of semi-crystalline grades of PLA. Some of the critical issues in PLA processing include the control of the crystallization kinetic and the degree of crystallinity of the final product. In general, crystallization kinetic of PLA is very slow: for example an amorphous state can be easily obtained by quenching from the melt. First attempts to duplicate the previous low-density foam results but using this time a semi-crystalline PLA resin were unfortunately not very successful, since premature crystallization took place inside the extruder and the die as the temperatures were approaching the desired adequate processing window.

It has been previously reported in two separate studies that carbon dioxide can promote the crystallization of the PLA resin. Sato and co-workers [2] reported CO_2-induced crystallization for PLA samples exposed to at least 1-2 MPa in the 40-60^{o}C range, which corresponds to a CO_2 content of roughly 3-5 wt%. Similarly, Xu *et al.* [3] observed crystallization of PLA at room temperature, for a polymer sample charged with at least 7-8 wt% of CO_2. The plasticization of the carbon dioxide under these conditions was such that the glass temperature was lowered below the test temperature. Enhancement of the mobility of the PLA chains in the rubbery state due to the presence of dissolved gas molecules enables thus the formation of crystallites, although the reported crystallization process remained still pretty slow and took a few hours.

Despite the difficulties inherent to highly volatile gases such as carbon dioxide, Takada *et al.* [4] reported interesting results on the crystallization kinetics for PLA/CO_2 systems, using a high-pressure differential scanning calorimeter (DSC). This study reported that the crystallization rate was accelerated by the presence of CO_2 molecules in the crystal-growth controlled region (low crystallization temperature region, associated with decreasing chain mobility), whereas it was depressed in the nucleation-controlled region (high crystallization temperature region, associated to the higher mobility of the polymeric chains). So the crystallization process was not only shifted to a lower temperature in presence of a plasticizer, but it was also speeded up. It was also reported in the same study that, while the presence of CO_2 did not change the crystalline structure for CO_2 pressures up to 2 MPa, it rose the crystalline content to higher levels. For example, a CO_2 saturation pressure of 2 MPa was found to increase the crystallinity from 26% (neat PLA) to more than 45%, at a crystallization temperature of 140^{o}C.

Unfortunately these experiments based on a high pressure DSC did not allow to separate the effect of pressure from that of the concentration of dissolved gas molecules into the polymer sample, since the concentration was pressure dependent in this experimental set up. The situation prevailing during foam extrusion implies a set amount of dissolved carbon dioxide, with high pressure variations throughout the extruder and the die. Therefore, it is of great interest to determine quantitatively the respective influence of hydrostatic pressure and dissolved CO_2 content on the crystallization kinetic of PLA. In order to fulfill these objectives, crystallization kinetics were investigated using a unique device combining ultrasonic characterization and volumetric measurements, with independent control of gas concentration and hydrostatic pressure.

EXPERIMENTAL PROCEDURE

Materials Two grades of PLA resins from NatureWorks^{TM} were used in this study. The first one is a completely amorphous copolymer having a D- content of 9.85% (grade 8302D, coded aPLA in this work). It was used mainly to investigate the degree of plasticization achieved with carbon dioxide, i.e. the decrease of the glass transition temperature. The second one, a semi-crystalline resin with a D-content of 4.25wt.% (grade 2002D, coded cPLA), was used for the crystallization kinetic study. Both materials were dried for around 8 h at 50^{o}C prior to experiments. Commercial grade of carbon dioxide was used without any further purification.

Differential Scanning Calorimetry (DSC) DSC experiments were carried out on neat cPLA (without CO_2) in a TA-DSC Q1000 apparatus. Specimens were first heated up to 200°C and maintained at that temperature for 10 min to ensure complete melting of the crystalline phase, and then were cooled down at a rate of -40°C/min to the selected crystallization temperature. Sufficient time was allowed to complete the crystallization stage (~12 h).

Ultrasonic Measurement Experiments were carried out using a unique device previously developed in our laboratory, which is described in details elsewhere [5]. Basically, waves of small amplitude but high frequency (typically 2.5 MHz in our case) are propagated through a confined polymer sample (3 mm-thick cylindrical samples with diameter of 32 mm) and their propagation characteristics (sound velocity and attenuation) are measured as a function of controlled pressure and temperature conditions. Investigations of the crystallization phenomena, especially when pressure is applied or when gas or foaming agent is dissolved in the material, have been successfully undertaken through the monitoring of these ultrasonic properties [6, 7, 8]. In addition, the device gives access to the variation of specific volume, through accurate measurement of the sample thickness.

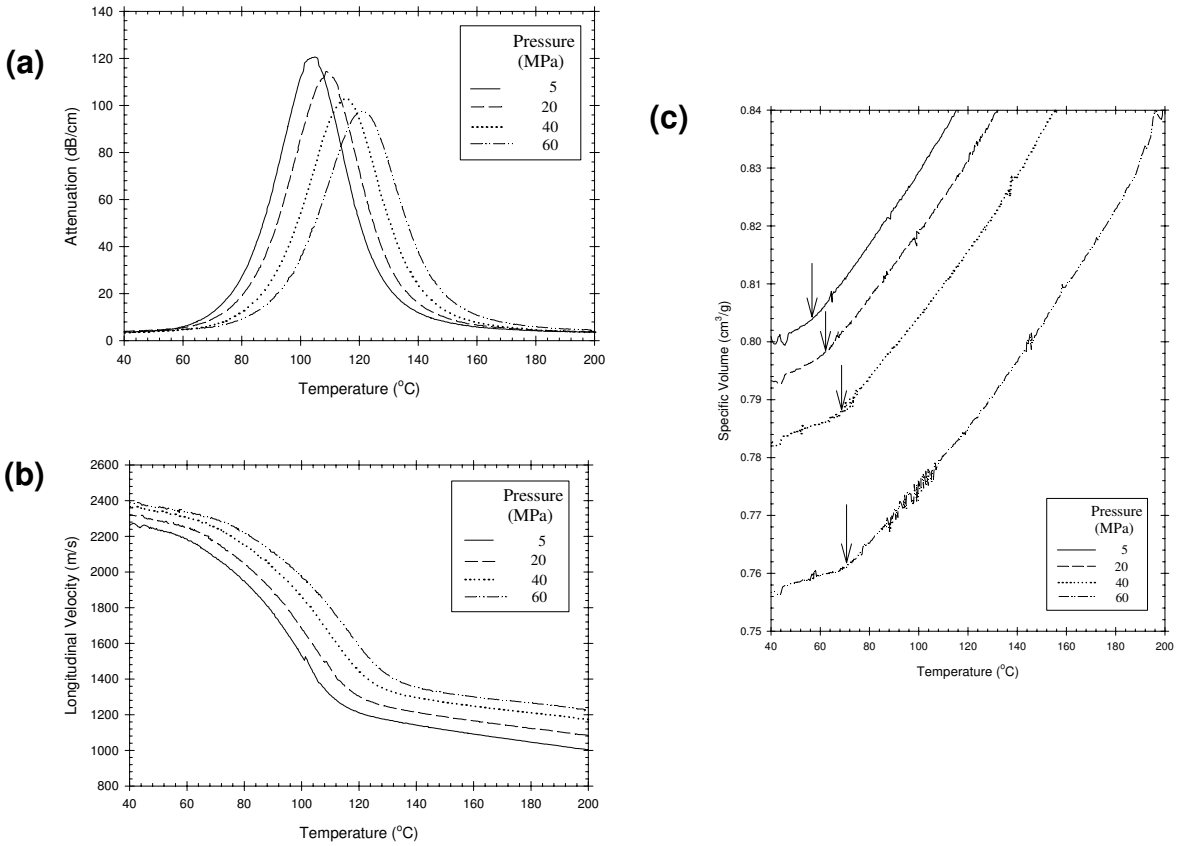

Figure 1: Evolution of attenuation, sound velocity and specific volume as a function of temperature for cPLA with various applied pressures (5 MPa (solid line), 20 MPa (dashed line), 40 MPa (dotted line) and 60 MPa (dashed-dotted line)). The samples were first heated at 200°C and then cooled down to ambient temperature at a rate of –2°C/min. The breakpoints on the specific volume curves area, indicated by the black arrows, correspond to the glass transition temperature (T_g).

Examples of typical results are provided in Figure 1 for cPLA, for temperature sweeps (cooling) performed under various hydrostatic pressures ranging between 5 and 60 MPa. Gradual shift of glass transition temperature of PLA with increased pressure (dependence of 0.26°C/MPa) can be seen on the specific volume curves (black arrows indicate the location of T_g). Similar temperature-shifts also occur for the ultrasonic properties. For example, the attenuation spectrum, which is characterized by the existence of a single relaxation peak (α-relaxation) related to the glass transition phenomena [9], is shifted towards higher temperatures when pressure is increased.

Figure 1 also illustrates that under these conditions (moderate cooling rate and high pressures), the cPLA as anticipated does not crystallize. The ultrasonic behavior (attenuation and velocity) of cPLA during the cooling run does not show any features corresponding to the crystallization of the material, as documented for various semi-crystalline polymers in previous studies [6, 8]. No evidence of crystallization was neither found with respect to the

volumetric behavior. In addition, crystallization of the cPLA sample did not occur during the cooling step down to the crystallization temperature for the experiments conducted in the presence of CO_2, despite the accelerated crystallization kinetic anticipated with carbon dioxide. Any crystal formation during the cooling ramp would have been accompanied by an abrupt change in the attenuation signal, which was fortunately not seen.

Crystallization kinetics Crystallization experiments were typically performed by first heating the polymer sample at 200°C for *ca.* 10 min, while maintaining the pressure at 20 MPa. Then the sample was quickly cooled down to the desired crystallization temperature (T_c), and the crystallization kinetics monitored under isothermal conditions, as displayed in Figure 2. Some PLA samples were previously charged with approximately 3.9 wt% of CO_2, by conditioning them in a pressure vessel filled with CO_2 (saturation pressure of 2 MPa) and maintained at room temperature for 24 h. Accurate concentration of CO_2 was later determined by weighing the sample before and after final degassing outside the device in a vacuum oven.

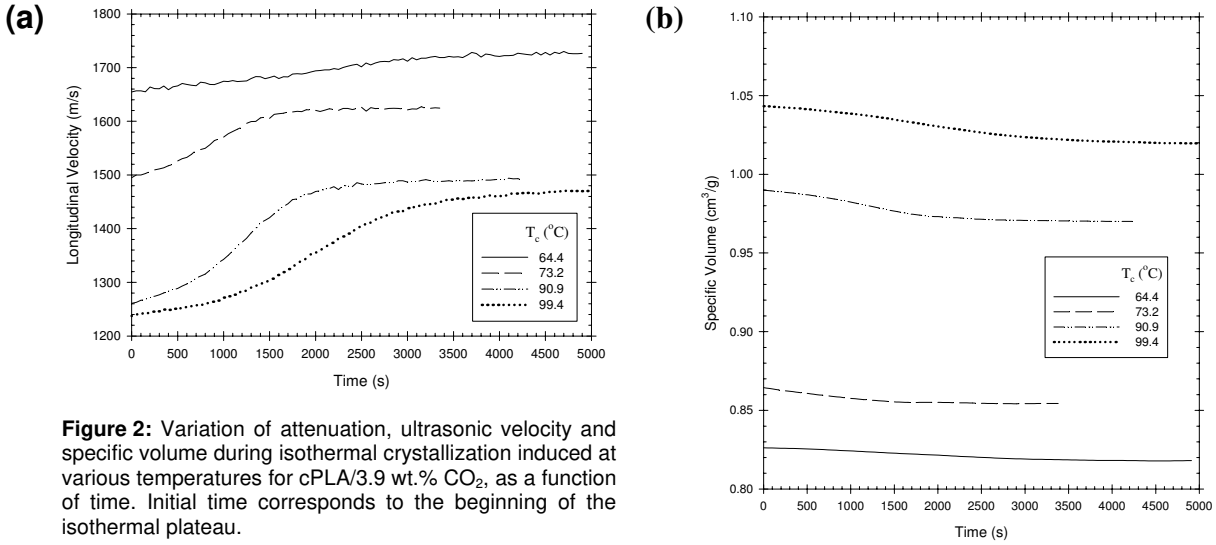

Figure 2: Variation of attenuation, ultrasonic velocity and specific volume during isothermal crystallization induced at various temperatures for cPLA/3.9 wt.% CO_2, as a function of time. Initial time corresponds to the beginning of the isothermal plateau.

Similarly to the classical approach that combines DSC measurements and the Avrami's model, the relative crystallinity was estimated through the variation of the specific volume by replacing the exothermic enthalpy with the specific volume [8]. Based on the observation that ultrasonic velocity and specific volume both show nice sigmoid curves ended by a plateau (see figure 2), the ultrasonic velocity (v_L) was also used to estimate the relative crystallinity. Interestingly, variation of velocity as a function of time is quite large which seems to indicate that this parameter is very sensitive to crystal formation, in comparison with variations in specific volume during crystallization which are rather small due to the small difference in specific volume of pure PLA crystal with respect to completely amorphous PLA [10]. Nevertheless, both sets of data were fitted with the following equations:

$$X_c(t) = \frac{V_0 - V_t}{V_0 - V_\infty} = 1 - \exp\left(-kt^n\right) \tag{1}$$

$$X_c(t) = \frac{v_t - v_0}{v_\infty - v_0} = 1 - \exp\left(-kt^n\right) \tag{2}$$

where V_0 is the initial specific volume, V_t and V_∞ are the specific volume at time t and at the final plateau, respectively; v_0 is the initial longitudinal velocity, v_t and v_∞ are the longitudinal velocity at time t and at the final plateau, respectively; k is the crystallization constant and n the Avrami exponent as usual.

Finally the crystallization kinetic is reported in this work through the values of the half-time of crystallization, denoted $t_{1/2}$. Conventionally when using DSC, the crystallization half-time corresponds to the time at which half the area under the isothermal crystallization peak has been generated, i.e. the time required to reach 50% crystallization (relative), X_c=0.5. In the present work, half-times of crystallization were calculated using the k and n

parameters obtained from the fitting process (Eqs. 1 and 2) and setting X_c=0.5, although this approach may emphasizes the early stage of crystal formation much more related to the nucleation stage:

$$t_{1/2} = \left[(\ln 2)/k\right]^{1/n} \tag{3}$$

RESULTS AND DISCUSSION

Effect of CO_2 on Plasticization

Representative plots of the attenuation for completely amorphous aPLA samples are shown in Figure 3 for temperature sweeps between 200 and -50°C (during cooling) and at various concentrations of CO_2. This figure illustrates a well-known result that the presence of dissolved CO_2, which increases free volume, affects the mobility of the polymer chains, such as a plasticizer usually does. This results in significant shifts of the α-relaxation peak to lower temperatures. For instance, the peak maximum shifts from 110°C to ca. 45°C when 10 wt.% of CO_2 is dissolved in the PLA, which indicates the strong plasticization induced to the material by CO_2.

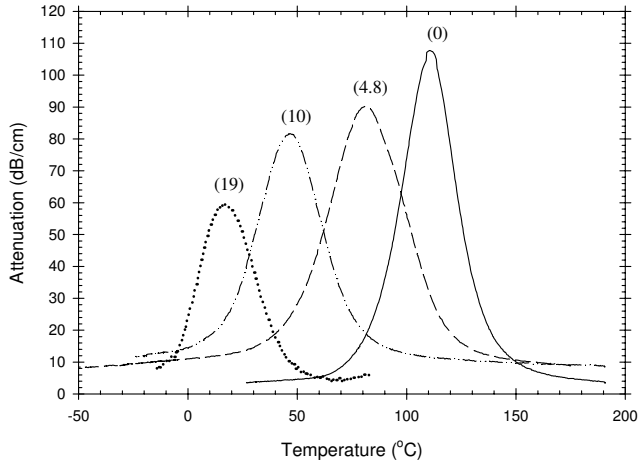

Figure 3: Evolution of the attenuation of aPLA (100% amorphous) during temperature sweep from 200°C to –60°C with various CO_2 contents. The numbers in parenthesis above each relaxation peak correspond to the concentrations of CO_2 (wt.%) in the samples. The pressure was maintained at 20 MPa throughout each experiment.

In our previous study on foam extrusion of amorphous PLA [1], the extent of plasticization induced by carbon dioxide has been estimated in-line using two different techniques: viscosity measurement and ultrasonic response. Plasticization was approximated as a decrease in the glass transition temperature T_g by -6 to -8 °C/wt% of CO_2. This result compared well to the plasticization effect on polystyrene using the same physical foaming agent, i.e. -8°C/wt% CO_2.

Figure 4 summarizes the results for the T_g depression of PLA as a function of CO_2 weight content, as determined from different methods: breakpoint in the specific volume during cooling, temperature corresponding to the maximum of the attenuation peak (denoted T_{max}) and estimates obtained from a model developed by Chow [11], with the lattice coordinate number, z, set equal to 1 and 2 for comparison purpose. The T_g depression curve estimated from the model with z = 2 exhibit a good correlation with the experimental points obtained from the breakpoint in V_{sp}.

For CO_2 concentrations below 5 wt.% CO_2, the curve obtained from T_{max} closely matches the T_g depression derived from the specific volume. However, at higher CO_2 content greater, a large discrepancy occurs. Considering the surface area of the relaxation peak, which is related to the relaxation intensity, we note that this area decreases for CO_2 concentrations above 5wt% (Figure 4b), indicating a decrease of the energy dissipated during relaxation. It is usually expected that, despite the change in height and width of the relaxation peak, its surface area should not change significantly with the concentration of the plasticizer. We thus can suspect that a particular phenomenon is occurring for PLA charged with a CO_2 content higher than 5wt%.

Such concentration threshold was also observed during the foam extrusion trials based on the amorphous PLA, with adequate expansion occurring only above 5-6 wt% of CO_2. This could be interpreted as intermolecular and/or intramolecular interactions of PLA chains becoming weaker because of the high concentration of CO_2, with enhanced lubrication of the polymer chains that eases the expansion process.

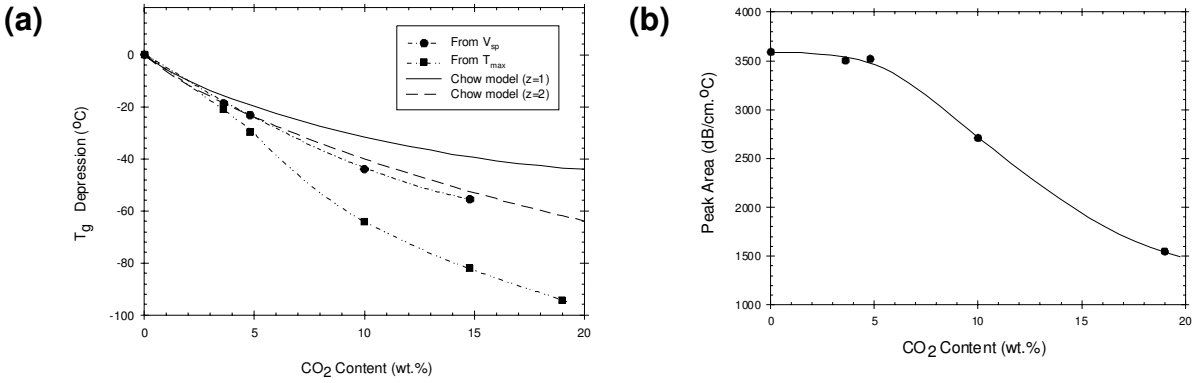

Figure 4: (a) Depression in glass transition temperature (ΔTg) estimated using various methods as a function of CO_2 content for aPLA. Experimental points were obtained either by ultrasonic measurements (peak maximum temperature in attenuation signal) or by volumetric measurements (breakpoint in specific volume curve). Chow model was used for comparison purpose with different values of z. (b) Evolution of the relaxation peak area observed in the attenuation response as a function of CO_2 content for aPLA. The lines are only guides for the eyes.

Crystallization of PLA

First, as displayed in Figure 5a, there is a very good agreement between the results for $t_{1/2}$ obtained from variation in ultrasonic velocity with those from volumetric change, for the two sample sets (with and without CO_2). Determination of crystallization kinetic has been usually obtained from volumetric or enthalpic measurements. Previous studies have indicated that ultrasonic measurements can provide easily crystallization and melting temperatures for various polymers [6-8]. The results shown in Figure 6a clearly shows that the ultrasonic velocity can also be used with confidence to evaluate the crystallization half-times.

Effect of Pressure on Crystallization Kinetic

The results corresponding to the unplasticized cPLA (without CO_2) are compared with results obtained more classically by DSC measurements in Figure 5. It has been shown in the past that crystallization (isothermal conditions) is accelerated by high pressure [12]. This is confirmed by the differences observed on the $t_{½}$ curves where the minimum of $t_{½}$ is shifted toward lower temperature when the pressure is increased. $t_{½}$ is reduced by a factor two when pressure is as high as 20 MPa. Nevertheless, in absence of carbon dioxide, crystallization remains still pretty slow considering that the fastest result lies in the one hour-range.

Effect of CO_2 on Crystallization Kinetic

The impact of dissolved CO_2 on isothermal crystallization of cPLA was examined in details by using our ultrasonic device coupled with volumetric measurements. The differences in $t_{1/2}$-curves shown in Figure 5a for neat PLA and PLA+3.9wt.% CO_2, submitted to the same hydrostatic pressure (20 MPa), clearly illustrate the direct influence of CO_2 on the crystallization behavior.

When the PLA/CO_2 system is isothermally crystallized at a temperature lower than *ca.* 105°C, CO_2 enhances the ability of PLA to crystallize (small $t_{1/2}$). For instance, the crystallization half-times at T_c~82°C for samples containing dissolved CO_2 is more than one order less than that without CO_2. In addition, Figure 5a also suggests that CO_2 has a tendency to flatten the dependence of $t_{1/2}$=f(T_c) at the bottom of the curve, i.e. for T below 100°C. The minimum in

$t_{1/2}$ (maximum crystallization rate) can be considered as almost constant over a wider temperature range in presence of CO_2, than for the CO_2-free PLA sample. However, at higher crystallization temperatures CO_2 slows down crystallization kinetic.

These results are qualitatively consistent with those reported by Takada *et al*. [4]. They demonstrated using high pressure DSC and a different grade of semi-crystalline PLA that the crystallization rate was accelerated by CO_2 at T_c<130°C (self-diffusion controlled region) and depressed at higher T_c (nucleation-controlled region). Despite differences between temperature limits for the two regions, similar tendencies have been observed in our case using a completely different characterization technique. At high temperature, adding CO_2 reduces the driving force for crystallization. Melting point is also affected, as reported by Takada et al. Dissolution of CO_2 into PLA also lowers significantly the T_g of the amorphous matrix. This translates into an increase of the segmental mobility of the macromolecules even at low temperature, which makes the crystallization process much easier and faster.

Figure 5b depicts the effect of CO_2 on the evolution of fractional crystallinity as a function of time for T_c~100°C. The presence of CO_2 shifts the S-shaped curve to smaller times, and that unambiguously indicates an acceleration of the crystallization kinetic in this temperature range (self-diffusion controlled region).

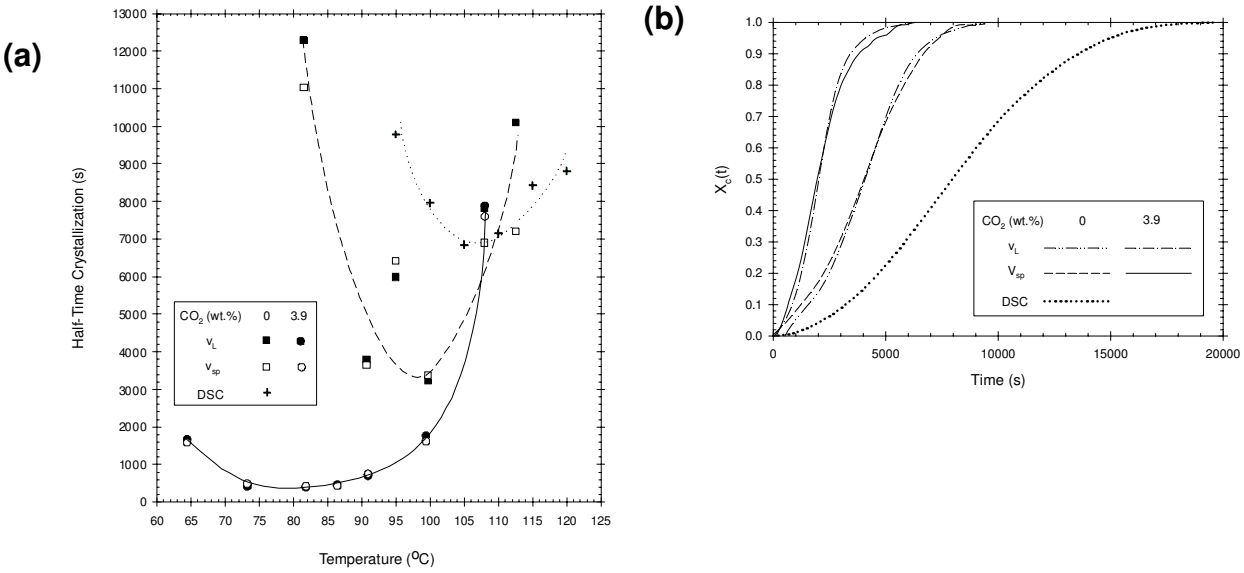

Figure 5: (a) Effect of CO_2 content on the crystallization half-time *($t_{1/2}$)* of cPLA as a function of temperature, with pressure set at 20 MPa, except for the DSC measurements (atmospheric pressure). Values of $t_{1/2}$ were determined either by DSC (cross symbol), by ultrasonic velocity measurements (solid symbol) or by specific volume measurements (open symbol). (b) Variation of fractional crystallinity as a function of time for a crystallization temperature of 100°C. Value of $X_c(t)$ obtained by ultrasonic, volumetric and enthalpic measurements are reported on the same plot for comparison purposes. Lines are only guides for the eyes.

Impact of CO_2-modified Crystallization Kinetics on Foaming

Obviously, the presence of carbon dioxide enhances considerably the ability of PLA to undergo crystallization. This kinetic is in addition speeded up by the hydrostatic pressure that needs to be maintained at a high level in order to keep the gas in a dissolved state. The concentration of CO_2 investigated in the present work was moderate (3.9 wt%), considering the high solubility reported for the CO_2-PLA system [2]. But taking into account the previous foaming results obtained with an amorphous grade [1], such low CO_2 concentration would not be sufficient to yield adequate expansion. Nevertheless, in the processing range of interest (90-100°C), the time required to initiate crystallization would have dropped to only a few minutes, from its notorious slowness without plasticizer.

Increasing the CO_2 concentration, as required for low-density foaming, would have two significant effects, unfortunately detrimental with respect to ease of processing. Higher content of CO_2 implies obviously higher pressures maintained in the extruder and die to prevent any premature gas-polymer phase separation, cell nucleation and foaming. Typically, based on solubility results [2], pressure should be kept to at least 7 MPa for 6-7wt% CO_2. However, peak pressures much higher than these values should be anticipated along the extrusion line,

especially in the pumping section. So the combined effect of pressure and CO_2 concentration would then make the crystallization process highly probable to occur.

In summary, strong affinity between PLA and CO_2 might play an adverse role in this foaming situation. Such affinity finds its source in the interaction between the carbonyl groups of PLA and carbon dioxide. High levels of carbon dioxide are thus required, which rapidly translate into strong plasticization and faster crystallization kinetics. This moves the processing window to higher but safer temperatures such as to avoid premature crystallization. However, a semi-crystalline polymer should exhibit specific rheological properties such as strain hardening to overcome the limitation imposed by a foaming window close to its crystallization point. To solve this issue, it has been proposed different approaches, such as reactive processing and nanocomposite compounding [13]. Otherwise, physical foaming agents other than carbon dioxide might thus be more appropriate for PLA foaming, and should be considered in future studies.

Conclusion

The effect of dissolved CO_2 on the glass transition temperature and the crystallization kinetics of PLA were investigated using an original device combining ultrasonic and volumetric measurements. Ultrasonic propagation parameters such as sound velocity and attenuation are sensitive to the structural state of the material and can be used easily to study the CO_2-induced depression in T_g as well as monitoring the crystallization kinetic with or without CO_2. Indeed, sound velocity was very sensitive to the crystallization of PLA. The results issued from velocity measurements can be favorably compared to the volumetric change method in determining the haft-time of crystallization.

Depression in the glass transition temperature was reported as a function of CO_2 content. The α-relaxation was investigated through attenuation measurements indicating that the energy dissipated during relaxation is strongly decreased beyond 5 %wt CO_2 content. A possible explanation is the weakening of intermolecular and intramolecular interactions of PLA chains with such CO_2 concentrations. This observation might explain some of the strange foaming behaviors previously reported on foaming amorphous PLA.

The crystallization rate in presence of CO_2 was found to increase essentially in the self-diffusion controlled regions. Results significantly differ from that obtained by DSC measurement on neat PLA at atmospheric pressure, and the faster crystallization kinetics observed even at moderate concentration of CO_2 explain the difficulties encountered during foaming of semi-crystalline grades of PLA with CO_2. Additional investigations on the crystallization kinetics should be conducted at higher CO_2 content, as well as using a different physical foaming agent.

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