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EFFECTS OF DISSOLVED CARBON DIOXIDE AND ORGANOCLAY ON THE CRYSTALLIZATION OF POLY(LACTIC ACID) AS PROBED BY ULTRASONIC MEASUREMENTS

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Abstract - While low-density foam extrusion of amorphous poly(lactic acid) (PLA) has been successfully performed, foaming its semi-crystalline counterpart still remains problematic, since blowing agents such as carbon dioxide affect significantly the crystallization kinetics of PLA. Similar kinetics enhancement has also been observed with the addition of organoclays.

The effects of dissolved CO_2 molecules on the crystallization kinetics of PLA, as well as the effect of addition of organoclay to the polymer, 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 and attenuation 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. Glass transition temperature was found to decrease non-linearly as the CO_2 concentration increases. Impact on foam processing is also finally addressed.

Introduction

Considerable attention and work have been devoted over the past few years toward opportunities to replace conventional synthetic polymers used in packaging applications due to environmental concerns. One of the promising candidates is poly(lactic acid) (PLA), a biodegradable polymer that can be made from renewable resources. PLA can be processed on conventional equipments, and is well suited for injection molding, blow molding, sheet extrusion, film forming and even foam extrusion.

In that latter case it has been reported promising results for PLA foams in the 20-30 kg/m^3 density range (see Figure 1) [1]. The amorphous PLA was foamed using 7-8wt% of carbon dioxide, an environmentally friendly physical foaming agent. Unfortunately, due to the low glass transition temperature of PLA, i.e. T_g being approximately 59°C, heat deflection temperature remained pretty low and the foam could not meet targetted requirements.

Foam extrusion of semi-crystalline grades of PLA was the next logical step in order to match the required mechanical properties. The end-material properties can be controlled through the ratio between the two enantiomers, L and D, obtained from the lactide monomer. Semi-crystalline grades are obtained with L-lactic acid content greater than 93% and crystallinity can be as up as 40%. Melting temperature is 169°C and cold crystallization temperature is roughly 110°C. Control of the crystallization kinetic and the degree of crystallinity of the final product remain challenging as the crystallization kinetic of PLA is known to be very slow. Surprisingly, foam extrusion of a semi-crystalline PLA resin was not very successful, since premature crystallization occurred inside the extruder and the die when temperatures were reduced to match the desired adequate processing window. The explanation to such phenomenon lies in the enhancement of the mobility of PLA chains in the rubbery state due to the presence of dissolved CO_2 gas molecules. CO_2-induced crystallization for PLA have been reported at very low temperature (25-60°C) by several authors for CO_2-charged PLA samples [2, 3].

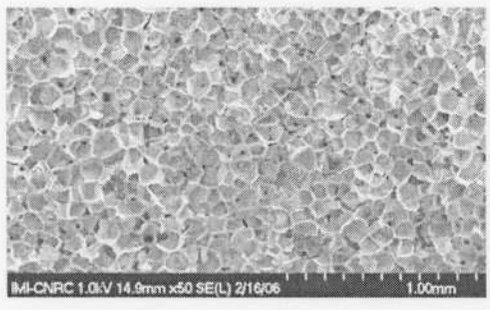

Figure 1. SEM photograph of a PLA foam, with density of 33 kg/m^3, extruded at 100°C using 7.3 wt% of CO_2 and 0.5 wt% of talc.

Crystallization kinetics for PLA/CO_2 systems has been the object of very few studies, due to the experimental difficulties inherent to such systems. In

one study, using a high-pressure differential scanning calorimeter (DSC), Takada and co-workers [4] reported that the combined effects of pressure and CO_2 content accelerated the crystallization rate in the crystal-growth controlled region (low crystallization temperature zone, where chain mobility is reduced), whereas it was slowed down in the nucleation-controlled region (high crystallization temperature region, where higher mobility of the macromolecules prevails). Similar results were also obtained by Reignier and co-workers using an original device combining ultrasonic and volumetric measurements [5]. Since sound velocity is very sensitive to the crystallization of PLA, the results on crystallization kinetics deduced from velocity measurements compared favorably to the volumetric change method in determining the haft-time of crystallization. In addition, this technique was well suited to isolate the specific contribution of the CO_2 concentration from that of the pressure on the crystallization kinetics modification. Such information is mandatory for foam extrusion since the process is based on a set amount of carbon dioxide being dissolved in PLA, with varying pressures along the extruder maintained above that of solubility equilibrium conditions. Contrarily to neat PLA at atmospheric pressure which exhibits slow crystallization, very fast crystallization kinetics were observed even at the moderate concentration of CO_2 investigated (3.9wt% CO_2) in the temperature range relevant to foam processing (90-100°C), which may explain some of the unexpected behaviors observed during the CO_2-foaming of semi-crystalline grades of PLA. In addition, emphasis was put on the high pressure needed to maintain the gas in a dissolved state that also speeded up the kinetics. Both contributions, gas content and pressure, would obviously be detrimental for any foam processing targeting low-density foams which would require high gas content and consequently, high pressures to prevent phase separation.

Moving the processing window to higher but safer temperatures in order to circumvent premature crystallization would unfortunately require specific rheological behaviors for the melt such as strain hardening to stabilize the cell structure until its solidification through the cooling-crystallization stage. Reactive compounding and addition of nanoclays [6] have been proposed as possible clues to solve the problem. In the present paper, the impact of nanoclays on crystallization kinetics will be evaluated using the same ultrasonic device as used in Reignier's study, and attention will also be paid to the combined effects with carbon dioxide.

Experimental

Materials

The polylactic acid used in this work, PLA 4032D, was supplied by Natureworks LLC. The D-lactic acid isomer content of 4032D is reported at 1.4 wt%, which leads to a PLA with a melting point at 160°C.

Materials were compounded in a Leistritz 34 mm twin-screw extruder operated at 150 rpm and 5 kg/h. Melt temperature used was 200°C. Cloisite 30B (Southern Clay) was added in a side-feeder located halfway toward the end of the extruder. PLA were dried according to supplier's indications prior the extrusion. A masterbatch containing 10 wt% clay was then let down to 2 and 4 wt% for testing and evaluation purpose.

Materials were characterized by transmission electron microscopy (Figure 2) and X-ray diffraction. (Figure 3) in order to access the state of intercalation and exfoliation of the nanoclays. As displayed in these figures, exfoliation has been achieved to a fair level, which should be highly beneficial for rheoloical and mechanical properties.

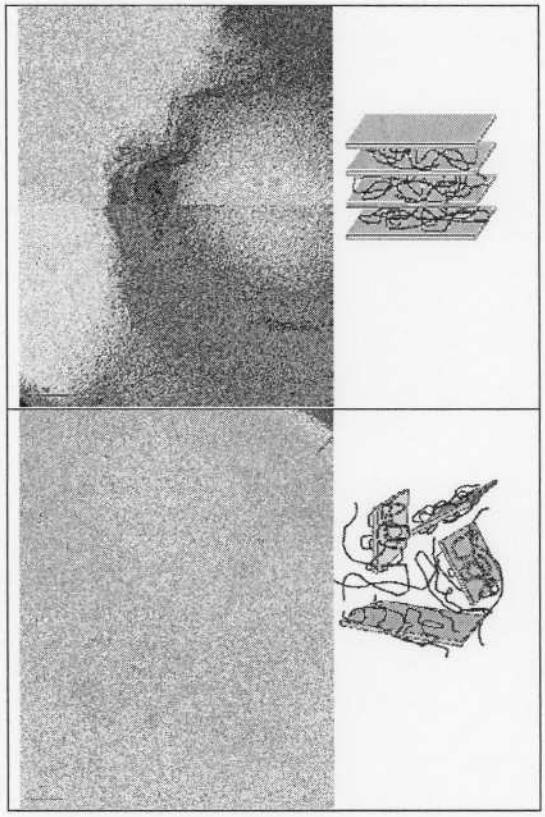

Figure 2: Transmission electron micrographs of melt extruded PLA nanocomposites containing 2wt% Cloisite 30B evidencing (top) intercalated structures and (bottom) exfoliated clay platelets. The scale bar in the top figure represents 50 nm while the bar in the bottom figure is 20 nm.

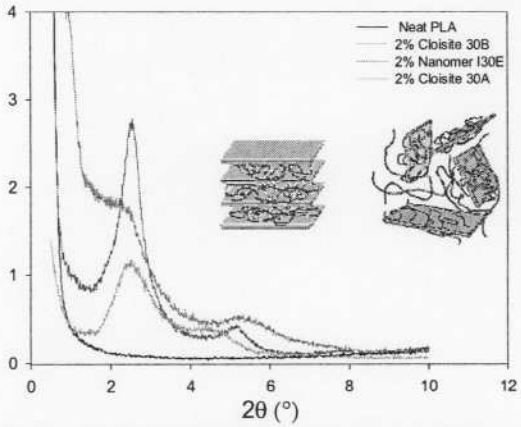

Figure 3: X-ray diffraction patterns of PLA nanocomposites based on different clays. The figure illustrates the significant level of exfoliation/intercalation observed in PLA/Cloisite 30B system as evidenced by the attenuation/displacement of the clay diffraction peak located at *ca.* 2θ ~2.5.

Ultrasonic Measurements

Experiments were carried out using a unique device previously developed in our laboratory, which is described in details elsewhere [7]. Basically, ultrasonic characterization of materials is based on the propagation characteristics (sound velocity and attenuation) of small amplitude high frequency waves (typically 2.5 MHz in our case) through a sample. Monitoring the ultrasonic parameters has been found to be very efficient to investigate crystallization phenomena, especially when pressure is applied or when gas or foaming agent is dissolved in the material [8, 9, 10]. In addition, the device allows monitoring of the thickness of the sample by using a linear variable differential transformer (LVDT) transducer and hence gives access to the specific volume. Figure 4 shows a schematic drawing of the measuring device.

Experiments were performed on cylindrical samples (32 mm diameter and 3 mm thick) that were molded from pellets directly into the sample holder of the ultrasonic measurement system under 20 MPa and at 200°C for *ca.* 10 min. For crystallization experiments without CO_2, the sample was then quickly cooled down to the desire crystallization temperature (T_c) at constant pressure.

Investigation of the effect of CO_2 on the crystallization of PLA requires the dissolution of CO_2 in the PLA matrix. For that purpose, some of the molded samples, obtained from quenching from the above molding conditions, were placed in a pressure vessel (Parr reactor) filled with CO_2 and maintained at room temperature for 24 h with various saturation pressures. After pressure release, the sample was quickly transferred to the ultrasonic measurement device where a pressure of 30 MPa was rapidly applied to prevent undesired foaming or gas loss. Maintaining this pressure, the temperature was increased up to 200°C, then the pressure was adjusted to 20 MPa and the sample quickly cooled down to the crystallization temperature. Accurate concentration of CO_2 into the PLA sample was later determined by weighing the sample before and after final degassing outside the device in a vacuum oven. The initial weight of the sample, immediately after pressure release and device opening (corresponding to the composition of the material during the experiments) was obtained by extrapolating at time zero the evolution of the weight as a function of time. Percentage error on CO_2 content is estimated to 0.05 wt%.

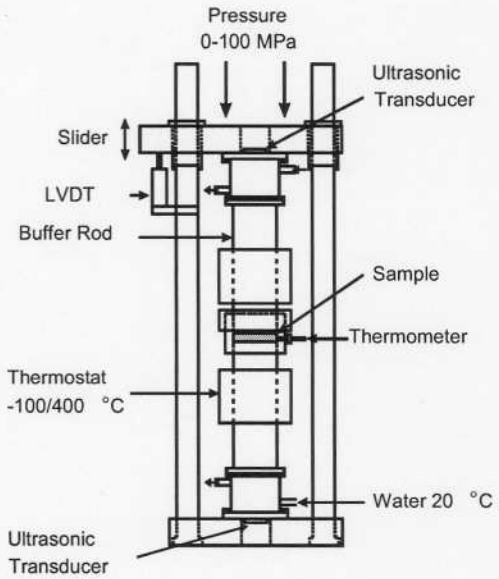

Figure 4: Schematic drawing of the ultrasonic device.

Results and Discussion

The isothermal crystallization of PLA was examined in details by using our ultrasonic device coupled with volumetric measurements, with or without the presence of dissolved CO_2 or/and nanoclay. Typical results are shown on Figure 5. The dependence of the attenuation signal with temperature and crystalline morphology is complex [11] and generally crystallization kinetics cannot be investigated by using the absolute attenuation as a parameter.

On the other side, ultrasonic speed and specific volume both show a nice sigmoid curve ended by a plateau. In addition, the beginning of velocity increase as well as the leveling off at the plateau coincide with the changes in specific volume.

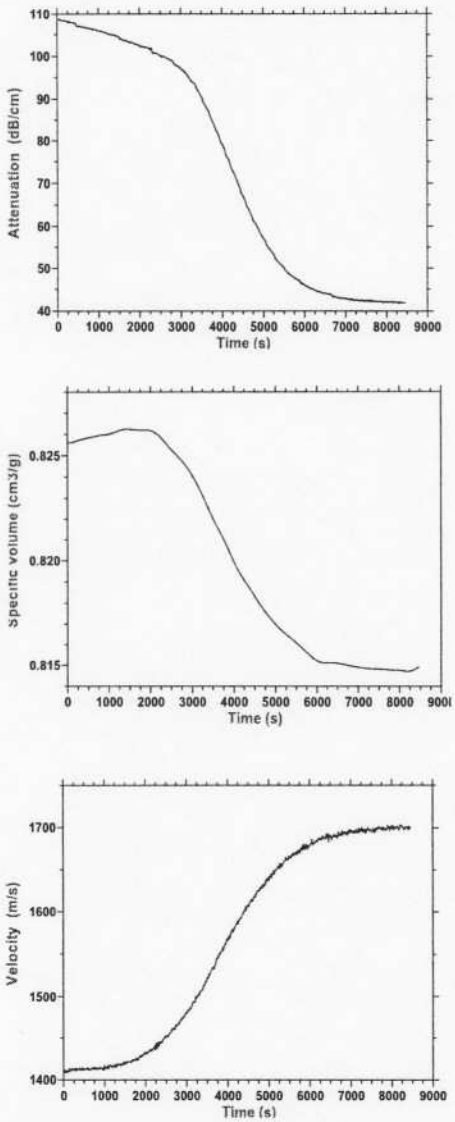

Figure 5: Evolution of respectively, attenuation, specific volume and sound velocity during isothermal crystallization of neat 4032D (T_c=102°C; P= 20 MPa).

Similarly to the classical approach develop by combining DSC measurements and Avrami's model, it has been shown in the past [9] that the relative crystallinity or fractional crystallinity can also be defined by variation of the specific volume by replacing the exothermic enthalpy with the specific volume, such as:

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

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. k is the crystallization constant and n the Avrami exponent as usual. Similarly, it is obvious to wonder whether the ultrasonic velocity (v_L) may also be used to estimated the relative crystallinity and hence the various kinetic crystallization parameters, according to the following relation:

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

where v_0 is the initial longitudinal velocity, v_t and v_∞ are the longitudinal velocity at time t and at the final plateau, respectively. Again, k is the crystallization constant and n the Avrami exponent. 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 and could therefore be used to follow easily crystallization kinetics. On the contrary, variations in specific volume during crystallization are rather small and the beginning of the final plateau corresponding to the end of crystallization is barely detectable with good accuracy, which is mainly due to the small difference in specific volume of pure PLA crystal with respect to completely amorphous PLA (ΔV_{sp}~ 0.023cm^3/g at room temperature and normal pressure) [12]. Nevertheless, both approaches were used to investigate the difference in crystallization kinetic for neat PLA without and with CO_2, and PLA nanocomposites without and with CO_2 according to the Avrami's model. 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. This specific approach can be extended to Equations (1) and (2) by taking the time corresponding to X_c=0.5 (relative crystallinity). Even if $t_{1/2}$ emphasizes the early stage of crystal formation much more related to the nucleation stage compared to the later stage of crystal growth that is more affected by chain mobility, it was decided to compare the crystallization kinetic of the various PLA/nanocomposites/CO_2 systems by investigating $t_{1/2}$.

The $t_{1/2}$ values obtained from variation in ultrasonic velocity compare very well with those obtained from volumetric change, for samples with or without CO_2. Usually determination of crystallization kinetic is obtained from volumetric or enthalpic measurements. Up to now, use of ultrasonic measurements was restricted to determination of the crystallization and melting temperatures of various polymers [8, 13], but previous results have clearly shown that v_L can also be used with success to evaluate the crystallization half-times [11]. The results are summarized on Figure 6 where the half-time values issued from sound velocity variations are plotted as a function of the crystallizing temperatures. Similar results were observed using the volumetric determination of $t_{1/2}$ and are therefore not reported here.

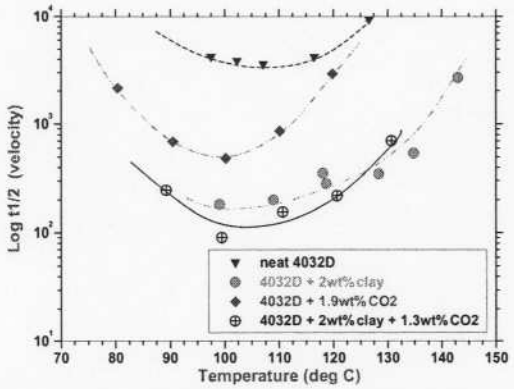

Figure 6: Crystallization half-time deduced from sound velocity as a function of crystallization temperature for the different materials (P= 20MPa). Lines are guides for the eyes only.

Three significant trends can be observed:

(i) The differences in $t_{1/2}$-curves shown in Figure 6 for neat PLA and PLA+1.9wt.% CO_2 clearly illustrate the influence of CO_2 on the crystallization behavior. For instance, the crystallization half-times at T_c~100°C for sample containing dissolved CO_2 is more than ten times less than that without CO_2. It should be reminded that the hydrostatic pressure applied to the sample was the same in both cases (20 MPa) and thus the difference between the two curves is strictly related to the presence of the relative small amount of carbon dioxide used throughout these investigations. Figure 6 seems also to indicate that CO_2 as the tendency to shift the minimum in $t_{1/2}$ (maximum crystallization rate) toward lower temperatures. Similar observations have been previously reported by Reignier and co-workers using a larger amount of CO_2 on a different grade of PLA [11].

(ii) The impact of nanoclays on the crystallization kinetics is highly noticeable: with respect to neat PLA, crystallization half-times are reduced by a factor of roughly 50. Thus material with only 2 wt% nanoclay exhibits much smaller $t_{1/2}$ than PLA with 1.9 wt% CO_2. But contrarily to the effects reported for carbon dioxide, the minimum of the parabolic curve for the PLA/nanoclay group remains practically unchanged compared to that of neat PLA. The shift observed with CO_2 could then be attributed to the plasticizing effect of the gas which acts as a diluant and thus improved mobility at lower temperature, while nanoclays purely acts as standard "nucleating agents" with no such effect of plasticization.

(iii) When a small amount of CO_2 (1.3wt%) is dissolved in the nanocomposite systems, the corresponding crystallization half-times remain practically of the same order of what is observed for material with only 2wt% nanoclay. A small effect can nevertheless be observed, with CO_2 cutting by half the half-time values and, as observed previously for the PLA/CO_2 systems, a slight shift to lower temperatures also occurs.

Finally, the main result that should be kept in mind from this study is that the combined contribution from CO_2 and nanoclays does not correspond to the sum of the individual effects, but is largely dominated by the presence of the nanoparticles. However, since both nanoclay particle structures were present in the polymer, intercalated and exfoliated platelets, we cannot ascertain for the specific contribution of each. Concentration of the nanoclays would also need to be thoroughly investigated with respect to its incidence on the amplitude of acceleration of the crystallization kinetics.

Obviously, any attempt to perform PLA foam extrusion using a system that incorporates nanoclays would yield the same difficulties as those encountered with carbon dioxide only. In addition, while presence of CO_2 maintains an acceptable processing window in the high temperature zone because of its plasticizing effect, nanoparticles accelerate the crystallization kinetics over the whole temperature range investigated, which could again be detrimental even at higher temperatures.

Conclusions

The effect of dissolved CO_2 and nanoclay on the crystallization kinetics of PLA was investigated using an original device combining ultrasonic and volumetric measurements. The results issued from velocity measurements can be favorably compared to the volumetric change method in determining $t_{½}$ in an Avrami analysis of the crystallization. This approach provide more sensitivity to the changes occuring in the polymer, and the ultrasonic set-up can easily accomodate polymeric systems incorporating both solid and volatile additives, with the pressure kept as an independent variable.

The crystallization rate in presence of CO_2 only was found to increase essentially in the self-diffusion controlled region, which correspond to the low temperature zone.

Nanoclays induced drastic changes on the crystallization half-time, and largely dominate the effect due to the carbon dioxide, although this latter remains slightly significative, especially with respect to its plastication effect.

It should be noted that this study only focused on the crystallization kinetics modified through the incorporation of various additives. It is expected that level of crystallinity may also be affected by the composition of the polymeric systems. Additional works are expected to address this issue.

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