

SUPERCritical FOAMING OF BIOSOURCED POLYMER

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Nowadays biosourced polymers keep attention of plastic manufacturers due to their eco friendly image. Application fields for this kind of polymer are getting wider from day to day. Classical processes as film extrusion or injection are now reachable but others as film blowing or foaming need more investigations. Polylactic Acid (PLA) features poor melt strength properties which limit its use in these last highly melt contributing processes.

The aim of this study is thus to investigate PLA chain modification and evaluate the processing improvement achieved. Polymer modifications have been performed by chain branching via reactive extrusion. An epoxy based additive has been introduced at different amount. Elongational rheology has been used to quantify melt strength enhancement of the modified PLA.

In order to evaluate the efficiency of melt strengthening, a foamability study has been conducted with supercritical carbon dioxide as foaming agent. The polymer modification ratio and the foaming temperatures are the two investigated key parameters. The complete characterization including density measurements and foam morphology provided useful information. Two specific foaming behaviours are observed regarding branching ratio and foaming temperature. Different competitive phenomena are described to explain foam nucleation and growth.

Key word: Carbon dioxide, bio sourced polymer, foaming.

INTRODUCTION

Poly(lactic acid) (PLA) is an attractive polymer in these days where oil resource depletion and environmental concerns are hot subjects. In order to cope with industrial expectations this bio sourced and biodegradable polymer must be as performant as conventional oil based ones. Different applications are yet reachable for this biopolymer [1] but its poor melt properties tend to keep it away from specific process such as film blowing or foaming.

The aim of the present study is to modify this biopolymer in order to improve its melt processability. In this way, a commercial PLA has been branched with an epoxide oligomer via reactive extrusion. The use of different amounts of modifier provided new polymers with specific rheological properties of melt. Melt strength enhancement has first been evaluated by extensional viscosity measurements.

Foaming is a typical process involving this kind of melt solicitation [2]. A foamability study was thus a pertinent final characterization to evaluate the targeted property enhancement. Batch foaming experiments have been conducted in a three step process. : i) A CO₂ impregnation at given temperature and pressure, ii) thermal stabilization at specific foaming temperatures and iii) foaming under controlled pressure release rate. Foamed samples have been characterized by density determination, morphological observation and thermal analysis.

MATERIALS AND METHODS

Poly(lactic acid) (PLA)

An injection grade of poly(lactic acid) (PLA 3051D®) provided by Natureworks® was used in this study. This polymer presents a glass transition at 60°C and a melting point at 156°C for a molecular weight (M_w) of $110 \cdot 10^3 \text{ g} \cdot \text{mol}^{-1}$.

Branching agent

A branching agent called Cesa Extend® was provided by Clariant®. This additive consists in PLA reacted with a certain amount of multifunctional epoxides (Joncryl® 4368 - BASF®).

Reactive extrusion

PLA 3051D® has been modified via reactive extrusion with the Cesa Extend® epoxy additive. Modifier has been introduced with amounts ranging from 1 to 3 wt. %. The resulting samples are respectively named PLA_1, PLA_2 and PLA_3. Neat PLA is used as reference and is identified as PLA_0.

A Clextral twin screw extruder (TSE) with an L: D ratio of 36:1 and $\varnothing=25\text{mm}$ was employed to perform reactive extrusion at 210°C. Reaction times were evaluated on small amounts of materials extruded with a DSM micro extruder by monitoring torque.

Extensional Rheology

A dynamic rheometer, Physica MCR (Anton Paar), equipped with a counter rotating cylinders module (SER) has been used to determine the extensional properties of the PLA samples. Rectangular plates (25x10x2mm) were clamped on the cylinders and heated at given temperature before starting the test. Tests have been performed at 180°C with an extensional rate of 5 s^{-1} .

Batch foaming

The batch foaming assembly consists in a high pressure cell with a capacity of 300 ml made by PARR Instruments (series 4560). A computer interface allows pressure and temperature driving and monitoring via a thermocouple, a pressure transducer and a back pressure pneumatic valve. The maximum temperature and pressure are respectively 350°C and 20 MPa. Foaming process was performed on 5x5x2 mm samples respecting the three specific stages:

- i) Saturation of the sample under supercritical CO₂ for 2 hours at 180 °C and 9.4 MPa.
- ii) Thermal stabilization at foaming temperatures during half an hour.
- iii) Sample foaming by quick pressure release ($dP/dt = 19 \text{ bars}\cdot\text{s}^{-1}$)

Density determination

Density determinations were performed by means of Archimedes' principle (buoyancy method). A double measurement of weight in air and in known density liquid allowed this evaluation.

Foam morphology

A Hitachi S3500N SEM was used to observe foamed samples. UTHSCSA Image Tool V.3 software allowed the cell size determination.

Thermal property

Thermal analyses were performed with the help of a TA instrument DSC (Q10 Serie). A ramp from 25°C to 200°C was performed on foamed samples at 10°C/min.

RESULTS AND DISCUSSION

Extensional rheology shows a very different rheological behaviour between neat and branched PLAs. The comparison of the different samples is reported in Figure 1. The modified PLAs reveal strain hardening which occurs from the start of the test for the highest branching ratio.

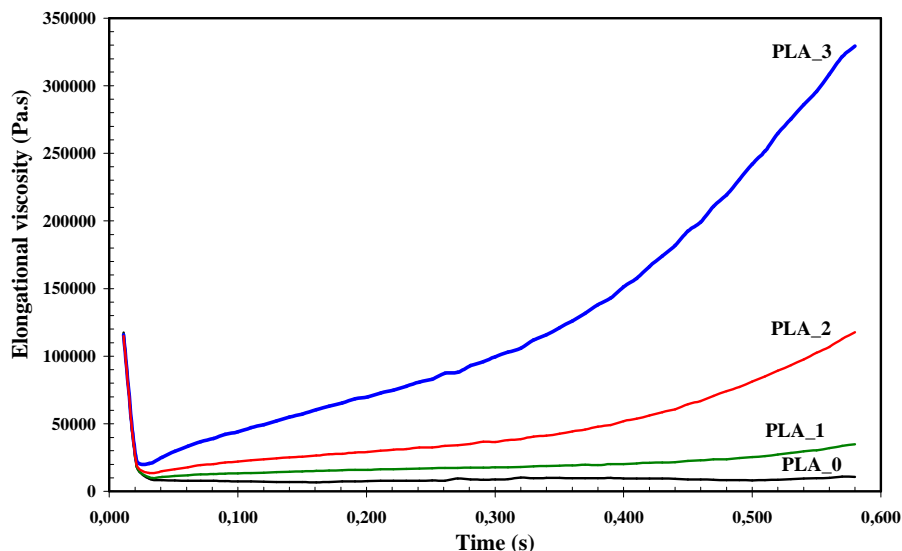


Figure 1 Extensional viscosity of neat and branched PLAs at 180°C and a strain rate of 5s⁻¹.

The batch foaming experiments provided samples with distinct physical aspects (as shown in Figure 2) as a function of branching ratio and foaming temperatures. Differentiation can be

made between neat or lowly branched materials (PLA_0 & PLA_1) and medium or highly branched ones (PLA_2 & PLA_3). This difference is also visible on the foams density evolution presented in Figure 3.

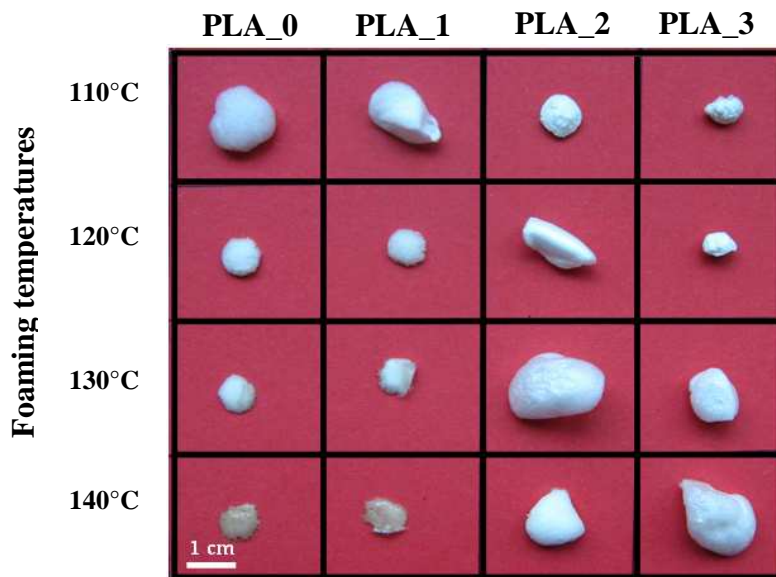


Figure 2 Foams obtained from neat and modified PLA's at different foaming conditions. Saturation stage is similar for all foamed samples (2H at 180°C and 9, 4 MPa).

Neat and lowly branched PLA

As seen on elongation curves, neat or lowly branched PLAs do not display any strain hardening behaviour. This lack leads to unfoamed samples at high foaming temperature. Melt is not strong enough to face up to gas expansion and cell coalescence occurs.

When the temperature decreases, the viscosity increases and samples can expand. The strain hardening is not compulsory for foaming under these conditions since the strain hardening is balanced by the viscosity increase. The Cells diameters are included in a macro scale and the cells concentration is low. The Foam density reported in Figure 3 reveals that density low values can be reached but a small increment of temperature drastically reduces the expansion by promoting cells collapsing.

Medium and highly branched PLA

PLA_2 density is optimally lowered for a foaming temperature of 130°C as seen on Figure 3. For PLA_3 samples, density still decreases from 120°C to 140°C. The both foams are macro cellular structured. Strain hardening limits cell coalescence at those high temperatures. An optimal efficiency is reached at a specific temperature depending on the branching ratio. Above this thermal condition cell coalescence occurs and density is getting up as seen for PLA_2 (Figure 3) at 140°C.

Lowering temperatures from optimal foaming conditions presented below tends to create high density micro cellular structures. Cooling material results in a matrix viscosity enhancement. This melt stiffness improvement leads to thinner and denser cells population by promoting nucleation in detriment of cell growth. For this kind of cell structure, strain hardening contribution can be neglected in front of the matrix viscosity.

The densification phenomena described above is shown to be more important for PLA_3 than for PLA_2 (Figure 2). It is known that the more a polymer is branched the more its thermal viscosity dependence is important. Melt stiffness thermal sensitivity is thus enhanced by increasing branching ratio.

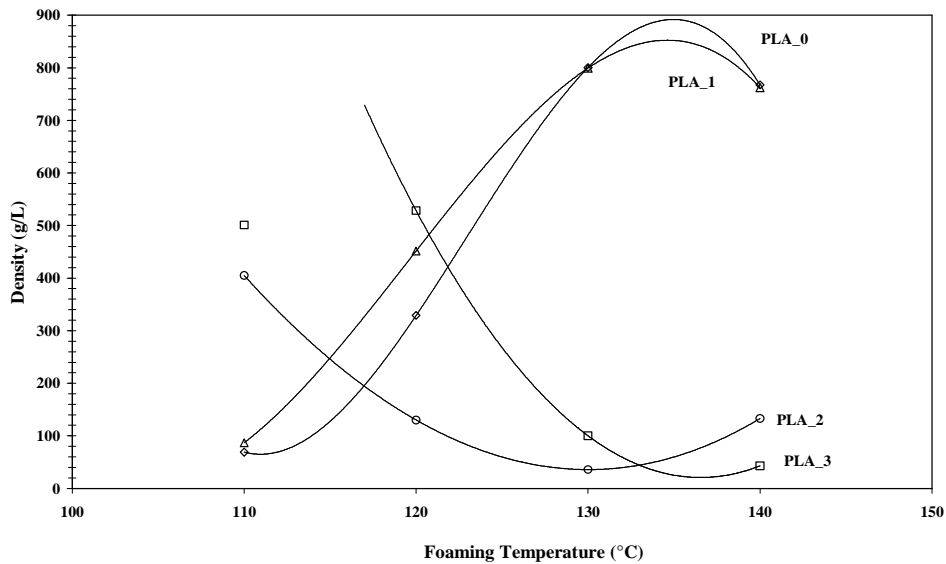


Figure 3 Foam densities obtained from neat and modified PLA's at different foaming temperatures. Saturation stage is similar for all foamed samples (2H at 180°C and 9, 4 MPa)

Crystallinity impact on foaming

As described above, the neat PLA used in this study is a semi crystalline polymer. Different researches have shown that CO₂ impregnation of polymer can induce crystallisation and result in highly nucleated foams [3, 4]. Thermal analyses presented in Figure 4 bring information about crystallinity of the foamed materials. Neat and lowly branched samples remain amorphous while other samples crystallise.

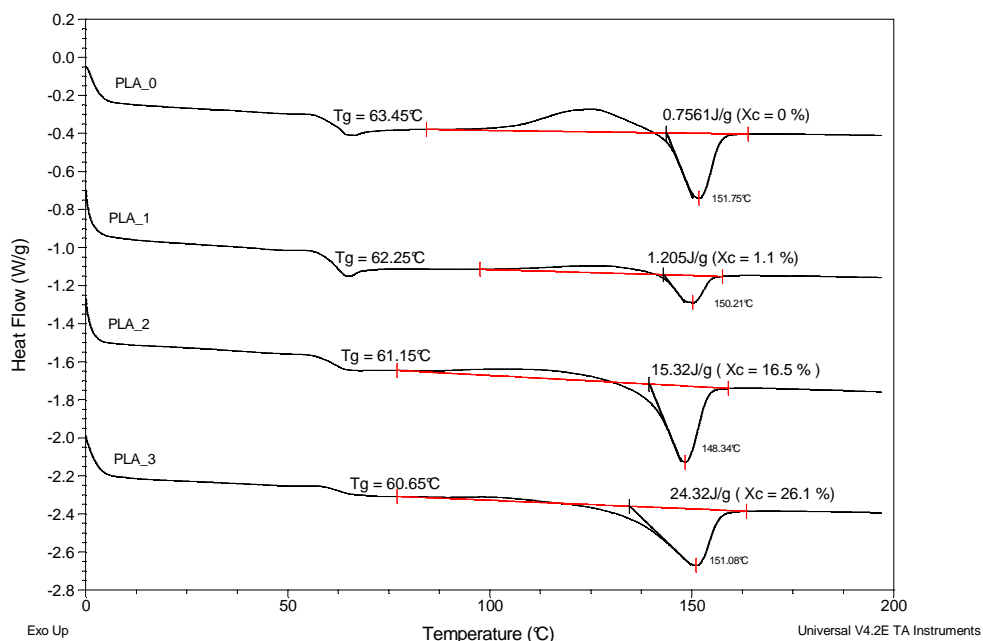


Figure 4 DSC thermograms of PLAs foamed at 120°C (1st heating at 10°C/min)

Such crystallinity level could influence the foaming process. Cell nucleation presented as linked to melt stiffness can be enhanced by high crystal nuclei population. In order to investigate the crystallisation behaviour of each sample, a microscopic observation under polarized light has been conducted at 110°C during 20 minutes (Figure 5).

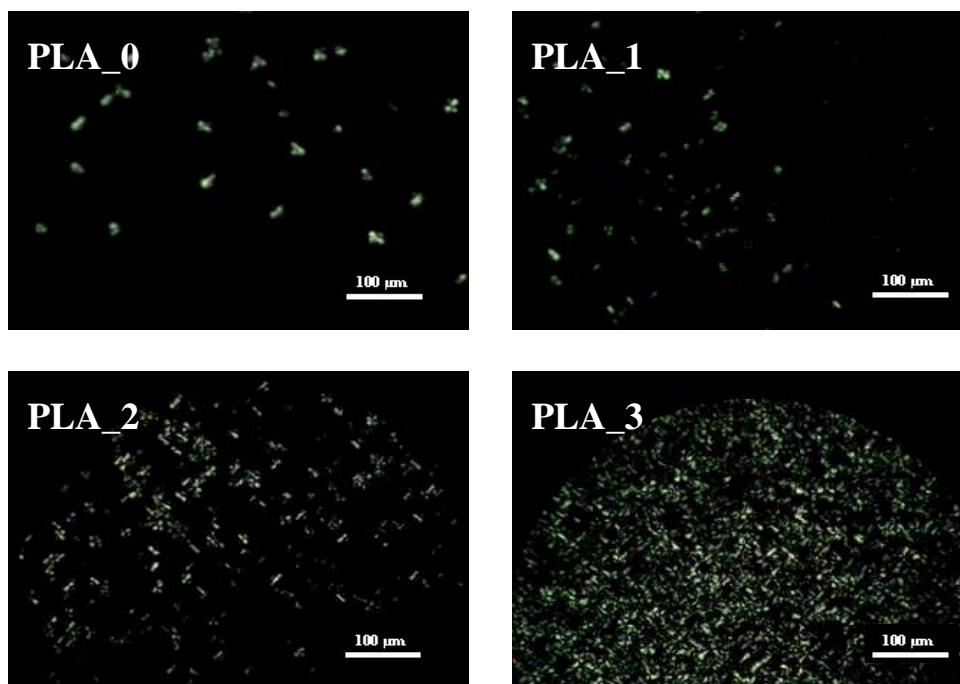


Figure 5 Micrograph pictures of a 20 minutes isothermal crystallisation at 110°C of neat and branched PLAs .

It is obvious that crystal density is improved with PLA branching ratio. This feature can be one of the keys governing the micro cellular foaming of highly branched PLA. Crystal induced strain hardening is also one other contribution that could explain the development of this thin and dense cell structure.

CONCLUSION

This work highlights that PLA melt strength can be easily tuned allowing its use in specific process such as foaming. Supercritical CO₂ foaming at different temperatures revealed that rheological improvement has specific effects on cells structure but depend on the process temperature. The crystallisation behaviour of the modified PLA can also be involved in the nucleation/growth process of PLA foams.

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