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EXTRUSION FOAMING OF SEMI-CRYSTALLINE PLA AND PLA/THERMOPLASTIC STARCH BLENDS

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Low-density open-cell foams were obtained by extrusion process from polylactic acid (PLA) and from blends of PLA with thermoplastic starch (TPS) using CO_2 as blowing agent. Two unexpected features were found. First, a 2D cavitation process in the fractured cell walls was unveiled. Elliptical cavities with dimensions in the 100-300 nm range were aligned perpendicular to large cell cracks clearly exhibiting 2D crazing prior to macroscopic cell rupture. Secondly, a significant crystallization rate increase associated with the CO_2 foaming of PLA was discovered. While the PLA used in this study crystallized very slowly in isothermal crystallization, the PLA foams exhibited up to 15% crystallinity providing evidence for CO_2 plasticization effect, and the biaxial stretching upon foam expansion provided conditions that could increase the crystallization rate by several orders of magnitude.

Introduction

Polylactic acid (PLA) and thermoplastic starch (TPS) are very attractive biobased polymers due to their availability, relatively low cost and their appealing physical and mechanical properties. Both of them are very versatile polymers, with properties that can be tailored as a function of their compositions. For PLA, the ratio between the two dimer stereoisomers, *L*-lactic acid and *D*-lactic acid, can be used to control the PLA properties and particularly its crystallinity. PLA comprising less than 7% of *D*-LA will be semi-crystalline with a crystalline level that increases with monomer purity to reach around 40% for the pure poly(*L*-lactide). Alongside PLA, thermoplastic starch is also a promising biobased material [1]. Once in a blend, their lack of affinity leads to extremely coarse blend morphologies and in all cases to very brittle materials [2]. The first successful compatibilization of TPS and PLA by adding maleic anhydride grafted PLA to the blends was reported recently [3]. This method was applied in the present work for TPS/PLA foamed blends.

Crystallinity is achieved currently in PLA in processes such as stretch blow molding and thermoforming where the large strains imposed at relatively low temperatures are sufficient to induce PLA crystallization without hampering with the material clarity. Inducing crystallization of PLA in processes that do not involve large amounts of biaxial orientation, as foaming process, is less trivial and is currently the subject of a lot of efforts in the scientific community. It is unclear whether PLA foams with significant crystallinity can be produced but one important feature of PLA, for our current purpose, is its increased crystallization rate in the presence of CO_2 at high pressures [4]. Extrusion foaming of TPS/PLA blends in which the PLA is the matrix and CO_2 the blowing agent has not been reported yet. The current work evaluates the foamability of PLA, PLA/TPS blends and the effect of interfacial modification using PLA-*g*-MA. The resulting foam's properties will be discussed in terms of cell morphology, density, and the crystalline content in the PLA will be analyzed through X-ray diffraction and thermal analysis.

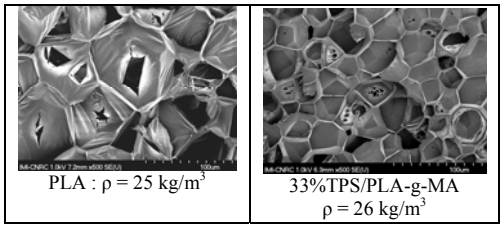
Experimental

The PLA 2002D, a semi-crystalline extrusion material composed of approximately 4% of *D*-lactic acid monomer was supplied by NatureWorks. It was dried at 65°C for a minimum of 8 hr prior to extrusion. The obtention of TPS and PLA/TPS blends and the ways of compatibilization are presented in [3]. The studied foams were obtained using a Leistritz 34mm co-rotating twin-screw extruder. The CO_2, 99% purity, was pumped as blowing agent into extruder barrel segment 7 and the rest of the extruder length was used to solubilize the blowing agent and to bring blend temperature to the desired final foaming temperature. The foams density was evaluated by water immersion method. SEM observations were carried out on cryogenically fractured foamed samples perpendicular to the extrusion direction. DSC analysis was used to evaluate the crystalline content of selected foams. For the initial crystallization measurements, the samples were heated at 20°C/min from ambient temperature to 200°C. Wide-angle X-ray (WXRD) diffraction patterns of the foamed products were obtained with an X-ray diffractometer (D-8, Bruker). The scanning was carried out at a rate of 0.03°/s in the angular region (2θ) of 2-40°. The foams were compressed at room temperature using a Carver Press for 10 min to collapse the foam structure and make dense bars.

Results and Discussion

Solubility measurements have shown that CO_2 is a highly soluble blowing agent for PLA (i.e 0.8%/MPa).

Low-density and high open cell content foams were obtained only when the CO_2 concentration exceeded 7%. PLA and blends of TPS/PLA were then foamed using a constant CO_2 concentration of 8% to investigate blend formulation effects on foam density and morphology. Figure 1 shows the morphology of pure PLA and TPS/PLA-g-MA foams. If in the first case the cell size was around 50μm, in the second case, at the addition of 33%TPS in a compatibilized blend the cell size decreased at 20μm.



PLA : $\rho = 25$ kg/m^3 | 33%TPS/PLA-g-MA $\rho = 26$ kg/m^3

Figure 1. SEM micrographs of foam of pure PLA and TPS/PLA-g-MA blends.

All obtained foams had a high amount of open cells. In Figures 2 and 3, higher magnification of foam morphologies for pure PLA and TPS/PLA blends are presented for the purpose of closely examining the cell opening phenomena. Figure 2a shows a single foam cell where one wall is ruptured. On the left part of the micrograph, is a section view of the cell walls. These are clearly less than 1μm thick. The higher magnification micrograph of a section adjacent to the inter-cell opening (2b) reveals a very interesting and peculiar structure.

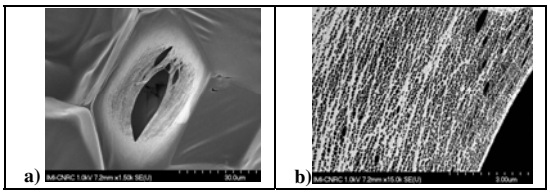


Figure 2. SEM micrographs showing a) one ruptured cell b) details of the cell wall close to the crack

The thin PLA wall is completely covered by extremely fine holes. These are slightly elongated in the direction of the crack and have a long axis that varied typically between 100 and 300nm. The holes were preferentially arranged in lines parallel to the main cell opening and the fibrils separating these holes were in the in the direction perpendicular to the main crack. Therefore, we can postulate that near the end of the foam cell expansion, when the cell thickness has been reduced to submicron levels and crazes formation appearing perpendicular to the main stress direction are resisted by the formation of PLA microfibrils. It has been postulated that crazes in semi-crystalline polymers are initiated in amorphous zones between crystal lamellae [5]. It is clear that the PLA crystallizes during foaming. In the case of TPS/PLA blend the rupture was different (Fig 3). Instead of a clear crack surrounded with small oriented holes, the wall shows a circular region where a more ductile failure occurred. The TPS phase, 200nm-1μm, appears as darker regions on these micrographs. The holes and fibrils are present only in the PLA phase leading to a network of very thin PLA fibrils separated by voids of uneven dimensions from 50nm to 400nm.

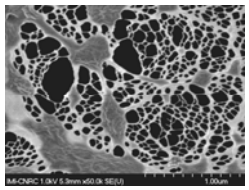


Figure 3. SEM details of the cell wall opening in 50%TPS/PLA (PLA containing 50%PLA-g-MA).

Table 1. Crystallinity fraction for foamed products.

	Crystalline content (%)	
	XRD	DSC
PLA	12.8	15.5
PLA with talc	6.9	15.8
33%TPS/PLA (50%PLA-*g*-MA)	13.5	19.5
50%TPS/PLA (50%PLA-*g*-MA)	14.5	22.8
Fully crystallized control	45	42

The results for XRD and DSC tests on foams are presented in Table 1. Both analyses supported the fact that significant crystallinity was developed during the foaming process. This significant crystallization rate increase could be described in relation with the combined effect of CO_2 plasticization and strain-induced crystallization.

Conclusion

PLA and TPS/PLA foams were obtained by extrusion in the presence of CO_2 as blowing agent. The foams had very low densities, high content of open cells and, most surprisingly, a high degree of crystallinity. The PLA used in this study had a very slow crystallization rate with crystallization half-time of several hours at its peek crystallization temperature of 100°C. However, X-ray diffraction and DSC analyses carried out on the foams indicated that significant crystallinity was developed in 2-3 minutes, during the foaming process. This was possible because of the high CO_2 concentration which highly plasticized the PLA, induced more chain mobility and accelerated the crystallization process. This finding opens the way to fabrication of PLA foams that could withstand much higher service temperatures than foams produced from amorphous PLA grades.

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