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Unveiling the role of elongational flow: Toward enhanced ductility in biopolymer blends

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ABSTRACT

In this work, the influence of the elongational flow on the microstructure and the ductility of a poly(lactic acid)/poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) blend was investigated. Anisotropic films were produced through cast extrusion and film blowing, and their morphology and mechanical properties were compared to those of an isotropic compression-molded sample. The results revealed that the application of the elongational flow is effective in inducing relevant modifications of the blend microstructure, passing from a droplet-matrix morphology for the isotropic sample to practically indistinguishable polymer phases in the anisotropic films. These processing-induced morphological alterations induced a brittle-to-ductile transition for both cast-extruded and blown films, which reached an elongation at break of 40 and 74 %, respectively.

1. Introduction

Growing concerns about plastic sustainability have driven increasing interest for renewable alternatives to fossil fuel–based polymers [1]. Among bio-polymers, poly(lactic acid) (PLA) and poly-hydroxyalkanoates stand out for their renewable origin and large-scale availability [2], despite some disadvantages still limiting their competitiveness with traditional plastics [3]. For instance, PLA exhibits brittleness and low impact resistance, whereas the narrow processing window of poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBH) restricts its industrial processability [4]. An industrially viable route to improve the biopolymers properties, while preserving their eco-friendly potential, is the formulation of blends [5]. However, polymer blends tend to develop phase-separated morphologies with weak interfacial adhesion, often compromising the mechanical properties of the resulting material [6].

It has been demonstrated that the polymer blend morphology can be profitably manipulated by varying the processing conditions and the type of flow applied during the processing [7]. In this context, the elongational flow has proven more effective than shear in deforming and breaking up the dispersed phase droplets, thereby promoting a substantial morphological refinement [8].

Here, the effect of the elongational flow on the morphology and the mechanical properties of a PLA/PHBH blend was assessed. In particular, anisotropic films were formulated through either cast extrusion or film blowing, aiming at evaluating the possible impact of the applied stretching on the material microstructure and ductility.

2. Materials and methods

The materials used were: poly(lactic acid) (PLA) 4042D (NatureWorks®Ingeo™) and poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHBH) IamNATURE-B6A13 (MAIP).

Two types of specimens were produced:

- Cast extruded films (PLA/PHBH_CE) by melt compounding 70 wt% of PLA and 30 wt% of PHBH in a twin-screw extruder (Process 11, Thermo Fisher) at 170 °C and 150 rpm, equipped with a flat die and a three-roll calendaring unit (take-up speed: 2 rpm, film thickness: 250–300 μm, ratio between the initial and final thicknesses: 3.5).

- Blown films (PLA/PHBH_FB) by further processing the melt-compounded PLA/PHBH 70/30 blend in a single-screw extruder (EUR.EX.MA Srl) equipped with a film-blowing head and a take-off unit (machine-direction draw ratio: 9.7, blow-up ratio: 2.93, film thickness: 20–50 μm, ratio between the initial and final thicknesses: 40–100).

Compression-molded specimens (PLA/PHBH_CM) were prepared using a hot-plate press (Collin Teach Line 200 T) at 100 bar and 170 °C.

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Before processing, the polymers were vacuum dried at 70 °C overnight.

An ARES (TA Instrument) plate-plate rotational rheometer was used for the frequency sweeps (temperature: 170 °C, N_2).

Morphological analyses were performed with an EVO 15 SEM (Zeiss), by fracturing the samples into liquid nitrogen and covering the surfaces with a sputtered gold layer.

An Instron® 5966 (Norwood, MA, USA) was used for the tensile characterization (crosshead speed: 1 mm/min). The tests were performed at least on 5 specimens and the results averaged.

3. Results and discussion

Fig. 1 shows the Cole-Cole plot of all the formulated PLA/PHBH samples. This kind of representation has been demonstrated to be highly sensitive in detecting phase separation in polymer blends, allowing elucidating the occurrence of multiple relaxation mechanisms attributable to the coexistence of dynamic entities differing in morphology, dispersion state, and degree of interfacial interaction [9]. Typically, single-phase materials display a regular and semicircular arc. Conversely, the presence of multiple phases introducing additional relaxation processes results in deviations from this ideal behavior, manifesting as a secondary arc. In polymer blends, the arc located in the low η' region (i.e. short relaxation times) is associated with the dynamics of the matrix macromolecules, whereas the high η' region is indicative of slower relaxation phenomena involving the deformation of the dispersed phase domains. Looking at Fig. 1, for both the isotropic and the cast extruded blends, in addition to the arc representing the relaxation of PLA macromolecules, a second arc appears in the region of long relaxation times. As mentioned before, this last can be attributed to the dynamics of the PHBH domains and the interactions between the polymer components. Nevertheless, for PLA/PHBH_CE the second arc is less broad, indicating a more homogeneous microstructure than the isotropic material. Differently, for the PLA/PHBH_FB sample, the Cole-Cole plot is in the form of a single arc, characteristic of a homogeneous single-phase system.

These results (as well as the curves of the complex viscosity and storage modulus reported in Figs. S1 and S2) suggest that the processing technology significantly affected the morphology of the blend; besides, especially for the blown film, the achievement of a more refined microstructure, with PHBH domains less impacting on the relaxation dynamics of PLA, can be inferred.

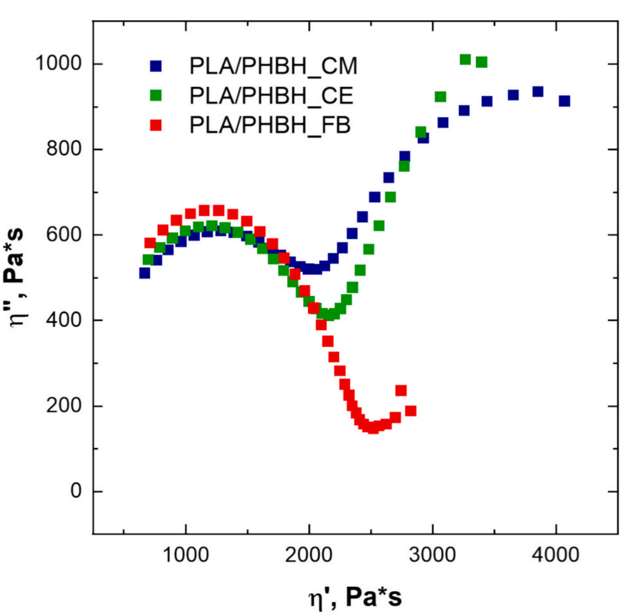

Fig. 1. Cole-Cole plot for all investigated PLA/PHBH blends.

These assumptions are confirmed by the SEM observations (Fig. 2). The compression-molded sample (Fig. 2A) shows the typical drop-matrix morphology of an immiscible blend, with roughly spherical PHBH domains embedded within PLA. Furthermore, some empty cavities, likely resulting from the pull-out of some PHBH particles during the fracturing, are noticed. In the cast-extruded film (Fig. 2B) the spherical domains of the dispersed phase are no longer clearly observable, as either the matrix or the PHBH particles appear elongated along the stretching direction. Additionally, the lack of empty spaces testifies the improvement of the interfacial adhesion between the two phases. The blend microstructure is even more homogeneous for the blown film sample (Fig. 2C). In this case the two phases are indistinguishable, and the blend morphology closely resembles that of a single-phase material. Elongational flow-induced morphology evolution in immiscible polymer blends is a documented phenomenon [10]. Specifically, when subjected to stretching, the domains of the dispersed phase are continuously deformed and oriented, and their final morphology depends on the intensity of the applied flow and on the stability of the deformed particles, as well. If the deformation action of the flow exceeds the interfacial forces, highly deformed and unstable elongated domains are obtained, which further evolve into smaller droplets through break-up events [8]. It can thus be deduced that the application of the elongational flow during cast extrusion and, even more, film blowing resulted in a substantial deformation of the second phase inclusions, with a progressive decrease of the average sizes of the PHBH domains passing from the isotropic to the anisotropic samples. This process results in a homogeneous microstructure where the second phase is practically indistinguishable through SEM analysis.

Finally, Fig. 3 reports the stress-strain curves, while in Table 1 the main mechanical properties are listed.

PLA/PHBH_CM presents a quite brittle tensile behavior, reaching an elongation at break of approximately 10 %. Nevertheless, this material shows increased ductility as compared to neat PLA and PHBH biopolymers (whose elongation at break is 4.9±0.6 and 2.7±0.4 %, respectively). Therefore, despite the drop-matrix morphology, the melt compounding step was effective in inducing a sort of synergic effect between the two phases. Notably, the processing of the blend through elongational flow-dominated technologies promotes a brittle-to-ductile transition. In fact, both films exhibit impressively higher elongation at break than the isotropic sample, along with improved elastic modulus and tensile stress. Considering that the crystallinity and the thermal behavior of the samples were not affected by the processing (see Fig. S3), this striking result can be explained considering the previously discussed elongational flow-induced evolution of the film morphology. In particular, the deformation of the dispersed phase domains and the consequent reduction of their size cause a significant increase in the matrix/s phase interfacial area, making more effective the stress transfer mechanism [11]. Furthermore, due to the stretching, PHBH particles are preferentially oriented along the same direction as the PLA macromolecules. Consequently, the deformed domains do not act as defects (as in the isotropic material) during the further deformation of the material, ultimately promoting improved deformability. Furthermore, while PLA/PHBH_CE exhibits a well-developed strain hardening behavior, the blown film sample shows a quite flat trend after the yield point. This finding can be attributed to the different degree of orientation of the matrix macromolecules in the two samples. In fact, in the cast extruded film, the strain hardening can be associated with the progressive orientation of the PLA chains during the tensile test. Differently, in the blown film, the matrix macromolecules attained a high degree of orientation already during the processing, and not appreciable further orientation occurs during the tensile test.

4. Conclusions

This work revealed fundamental processing-microstructure-

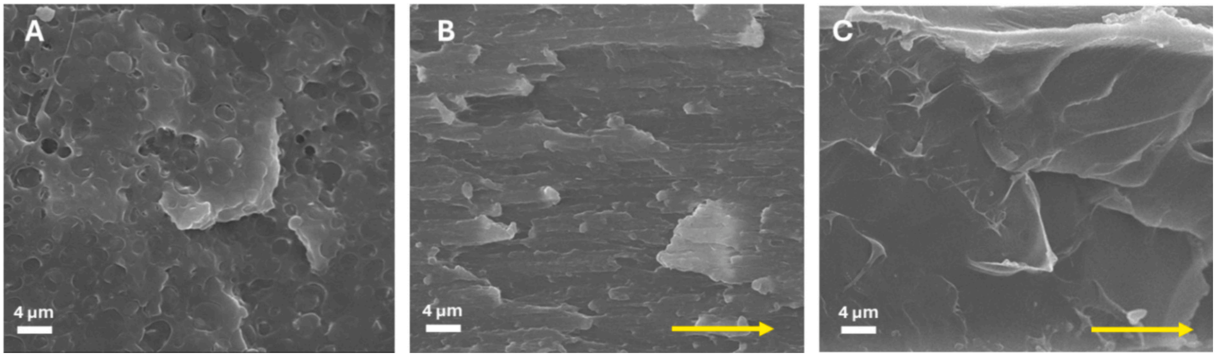

Fig. 2. SEM micrographs for (A) compression-molded, (B) cast-extruded and (C) film-blown PLA/PHBH samples (the arrows indicate the stretching direction in the anisotropic specimens).

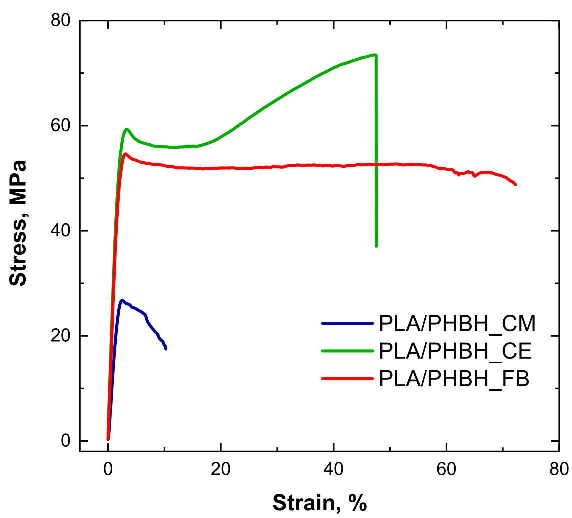

Fig. 3. Stress-strain curves for all investigated PLA/PHBH samples.

Table 1
Main tensile properties for all investigated PLA/PHBH blend samples.

Sample	Elastic modulus MPa	Yield stress MPa	Stress at break MPa	Elongation at break %
PLA/PHBH_CM	1676 ± 82	26.2 ± 2.1	25.3 ± 2.2	10.2 ± 2.8
PLA/PHBH_CE	3327 ± 76	60.3 ± 3.6	75.9 ± 2.5	43.1 ± 3.4
PLA/PHBH_FB	3549 ± 85	57.1 ± 4.3	52.7 ± 3.1	74.1 ± 3.6

properties relationships in PLA/PHBH blend films produced through industrially viable technologies. In particular, the effectiveness of the elongational flow in inducing significant morphological evolution and promoting mechanical property improvements was assessed. PLA/PHBH anisotropic films produced through cast extrusion and film blowing exhibited a more refined morphology (resembling that of a single-phase material in the case of the blown film) as compared to the compression-molded sample, which conversely is characterized by a droplet-matrix microstructure. Tensile tests demonstrated that these microstructural alterations promoted enhanced ductility for the blend films. In fact, PLA/PHBH_CE and PLA/PHBH_FB exhibited elongation at break of 43 and 74 %, respectively, showing a striking increase in deformability as compared to the isotropic sample (reaching about 10 % deformation) and to the inherently brittle PLA matrix.

CRediT authorship contribution statement

Rossella Arrigo: Writing – original draft, Supervision, Methodology, Formal analysis, Conceptualization. **Francesca Ianniello:** Investigation, Formal analysis, Data curation. **Chiara Gnoffo:** Investigation, Formal analysis, Data curation. **Giuseppe Trapani:** Investigation, Formal analysis, Data curation. **Alberto Frache:** Writing – review & editing, Supervision, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2025.139940.

Data availability

Data will be made available on request.

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