

MECHANICAL, RHEOLOGICAL AND THERMAL EVALUATION OF POLY(LACTIC ACID) (PLA) / MICRO FIBRILLATED CELLULOSE (MFC) PLASTICIZED BIOCOMPOSITES PRODUCED WITH FLAT DIE EXTRUSION AND CALENDERING

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Abstract: *The use of Micro Fibrillated Cellulose (MFC) as filler for polymeric matrices attempts an increasing interest both in academia and industry. In this framework, encouraging results have been obtained using plasticizers, as dispersing aids, during twin-screw extrusion that optimizes the process parameters and avoid MFC agglomeration. In this work, two commercial typologies of waterborne solution of MFC (Exilva and Celish) were melt-compounded in a PLA matrix through semi-industrial twin-screw extruder and calendered, producing films of 150 μm thickness. These films were mechanically and thermally characterized, moreover the migration of the plasticizer along the time was evaluated through analytical model and the diffusion coefficient was calculated.*

Keywords: Cellulose; PLA; biocomposites; Extrusion; Migration

1. Introduction

The need of finding new substitute materials, to minimize environmental footprint, is ever more pressing due to many ecological issues [1]. Polylactic acid (PLA) has gained interest because it can be synthesized from natural resources [2]. A common sustainable technique to improve the PLA performances is related to different strategies, such as the development of natural-filler-reinforced biocomposites [3]. Cellulose is known to improve barrier and mechanical properties of thermoplastic biopolymer films and currently special interest has been paid to PLA/microfibrillated cellulose (MFC) biocomposites [4] also for films applications.

As regards the production of PLA based films which can be carried out by flat die or blowing extrusion, the major drawback is represented from their excessive brittleness making them not commercially useful. To overcome this issue the mechanical flexibility of the PLA films can be improved through the addition of low-to-medium molecular weight plasticizers [5]. The choice of the most suitable plasticizer, especially in biobased applications, depends from the achievement of a good miscibility degree in order to avoid remixing, films opacity and, in

addition, its migration out of the film [6]. Moreover, the plasticizer migration also affects the final mechanical properties leading to a loss of flexibility and toughness [7].

Different approaches can be adopted to limit this phenomenon, filler addition is particularly interesting and, between the various nano- and micro-scale fillers available in commerce, cellulose is very attractive due to its well-known contribution in improving both the barrier and the mechanical properties of bio-plastics matrices [8,9]. This material is usually called microfibrillated cellulose (MFC), nano-fibrillated cellulose (NFC) or cellulose nanofibrils (CNF) and it is obtained as an aqueous suspension [10]. Nevertheless, by considering an exploitable industrial production of MFC based bio-composites, the critical drawback of cellulose agglomeration must be overcome to minimize its vulnerability to environmental attacks such as bio-damage, thermal deterioration and mechanical failure at the interface [11].

The aim of this study was to investigate mechanical and thermal properties, besides the plasticizer migration, of flat die extruded PLA based films reinforced with MFC as a filler using two different biobased plasticizers as dispersing agents (polyethylene glycol (PEG) and lactic acid oligomer (OLA)). Finally, the results have been compared after 50 days from the biocomposites manufacturing, evaluating the crystallinity and mechanical properties variations.

2. Materials and Methods

2.1 Materials

- Poly(Lactic Acid) (PLA), trade name PLA 2003D, purchased from Natureworks. Density: 1.24 g/cm³; molecular weight (MW): 200,000 g/mol; melt flow index (MFI): 6 g/10 min at 190 °C: 2.16 kg).
- Poly(ethylene glycol) (PEG 400) purchased from Sigma-Aldrich (CAS number: 25322-68-3; MW: 400 g/mol, density: 1.12 g/cm³; water solubility: 100 mg/mL).
- Lactic acid oligomer (OLA), trade name Glyplast OLA 2, provided by Condensia Quimica, (Barcelona, Spain) (ester content: >99%; density: 1.10 g/cm³, water content (ASTM E 203): maximum 0.1%; molecular weight: 500 g/mol).
- MFC Exilva F 01-L 10% kindly provided by Borregaard (Sarpsborg, Norway) with a solid content of 1.5–2.4% (viscosity - in H₂O 2% - ≥ 14,000 mPa·s).
- MFC Celish KY100S 25% purchased from Daicel Miraizu Ltd. (Osaka, Japan) (CAS number: 9004-34-6).

Both MFC, morphologically analyzed in a previous work [10] are characterized by long and thin fibers arranged in a three-dimensional network interconnected to each other.

2.2 Methods

2.2.1 PLA/MFC compounding and flat die extrusion

The accurate MFC feeding into the extruder through the addition of bio-based plasticizers, has proved to be very effective in avoiding agglomeration issues. Furthermore, the procedure, successfully adopted and illustrated in [10] was used. The extrusion compounding was carried out on a semi-industrial COMAC EBC 25HT (L/D = 44) twin-screw extruder (COMAC, Cerro

Maggiore, Italy). The formulations obtained and their relative compositions are reported in *Table 1*.

Table 1: Formulation names and compositions

Name	PLA (wt.%)	PEG (wt.%)	OLA (wt.%)	Exilva (wt.%)	Celish (wt.%)
P_O	85	-	15	-	-
P_P	85	15	-	-	-
P_O_E	83.3	-	14.7	2	-
P_O_C	83.3	-	14.7	-	2
P_P_E	83.3	14.7	-	2	-
P_P_C	83.3	14.7	-	-	2

For the extrusion, PLA was added in the main extruder feeder while the plasticizer/MFC emulsions were fed through a peristaltic pump at 2/3 of the screws length. A vacuum pump (degassing system) positioned in proximity of the end of the screw ensured an efficient water stripping. The strands coming out of the extruder were cooled in a water bath and then pelletized by an automatic cutter. The granules were then dried in a DP604–615 PIOVAN dryer (Venezia, Italy) at 50 °C for 12 h before their flat die extrusion. The flat die extrusion has been carried out in a second extrusion step adding a flat die head, while the water bath was substituted by a AMUT calendaring system. The temperature profile adopted in the extruder was the same used during the extrusion compounding with the flat die temperature set at 180°C °C. The correct homogeneity was obtained through a calendar apparatus regulated by setting the rollers cooling at 20 °C and the wind-up roll speed at 4 m/min. The obtained films were 20 mm width with a thickness of 150 µm.

2.2.2 Biocomposites characterization

Melt flow rate (MFR) measurements were carried out according to UNI EN ISO 1133 by a CEAST Melt Flow Tester MF20 (INSTRON, Canton, MA, USA). Five grams of pellets obtained by upscale extrusion were heated at 190 °C in a barrel and pushed through a normalized die (2.095 mm) under a constant load of 2.16 kg.

Tensile tests were carried out on an INSTRON universal testing machine model 5500R (Canton, MA, USA). The machine was equipped with a 100 N load cell interfaced with Merlin software. The specimens for tensile testing were shaped into ISO 527-2/5A dumbbell specimens with a manual Elastocon EP 08 cutting press (Elastocon, Brahmult, Sweden). The initial grip separation was equal to 25 mm and the deformation rate was set at 50 mm/min. Samples were cut in the machine direction (MD) and cross direction (CD) to evaluate the differences in the mechanical properties along the flow direction collected respectively by the wind-up roll (MD) and transverse (CD) direction. At least five specimens were tested for each formulation reporting the average values. The crystallinity degree was determined by calorimetric analysis using a Q200 TA-Instruments DSC equipped with an RSC cooling system. About 10-15 mg of material was cut

from the calendered film and it was sealed inside aluminum hermetic pan. In order to take into account the crystallinity of the system after the calendaring process while monitoring its variation during the storage time, only the first heating run was considered. In particular, the following thermal program was adopted: heating from room temperature at 10 °C/min up to 190 °C. The melting temperature (T_m) and the cold crystallization temperature (T_{cc}) were registered at the maximum of the melting peak and at the minimum of the cold crystallization peak respectively. The enthalpies of melting (ΔH_m) and cold crystallization (ΔH_{cc}) were calculated integrating the areas under the corresponding peaks. The crystallinity percentages (X_{cc}) reached by the PLA were calculated as follows [12]:

$$X_{cc} = \frac{\Delta H_{m,PLA} - \Delta H_{cc,PLA}}{\Delta H_{m,PLA}^{\circ} \cdot wt.\%_{PLA}} \quad (1)$$

Where $\Delta H_{m,PLA}^{\circ}$ is the melting enthalpy of 100 % crystalline PLA and is equal to 93 J/g [13] while $wt.\%_{PLA}$ is the total mass fraction of PLA in the formulation.

To evaluate the weight loss of films due to the plasticizers migration, three pieces of film for each formulation (40 x 40 x 0.2 mm) were put between two paper sheets. To accelerate the migration process making it more severe, the manufactured samples were kept in a ventilated oven at 60 °C (above the material T_g). Day by day the films were weighed to estimate the plasticizer weight loss over time. The film weight loss as a function of time was determined according to the following relationship [5]:

$$\% wt_{loss} = \frac{w_{t,film} - w_{t0,film}}{w_{t0,film}} \cdot 100 \quad (2)$$

where $w_{t,film}$ is the film weight at the time t and $w_{t0,film}$ is the film weight at the beginning of the test ($t = 0$).

The MFC addition effect on the plasticizer migration was quantified according to the equations and procedure explained by Aliotta et al. in [5].

3. Results

3.1 Melt flow rate

A useful test to evaluate the processability of the studied formulations is the mass flow rate analysis. From *Figure 1* it is possible to observe that, as expected, the fluidity of the plasticized matrices was much higher than those of all biocomposite formulations. More specifically, the PLA matrix plasticized with OLA showed a tremendous fluidity at 190 °C with a rather low melt strength and was hardly used for filming applications at such temperatures.

The melt strength was considerably improved with the inclusion of MFCs. The melt flow rate of the Celish–MFC composite was even 5 times lower than that of the Exilva–MFC. This result demonstrates that MFC can impart strengthening to the melt, but is necessary to verify if this viscosity increment can be associated with a better distribution of the cellulosic particles in the matrix and a better shielding action against plasticizer migration, going also to observe how this behaviour affects the mechanical properties

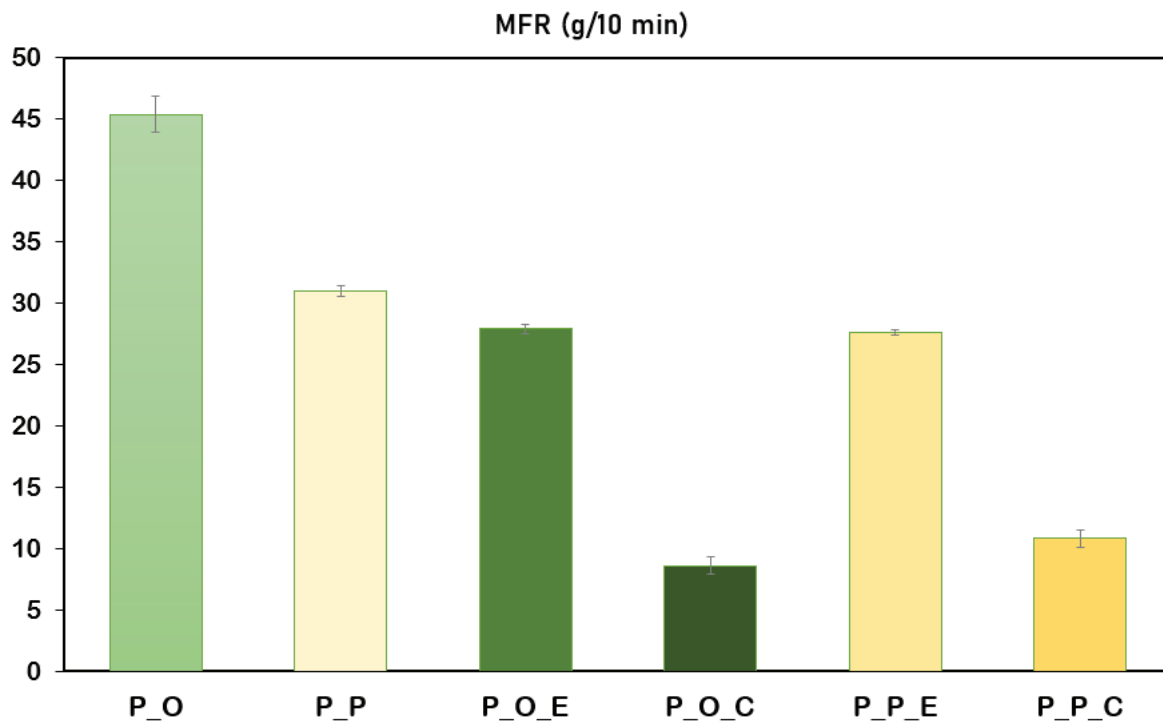


Figure 1. Mass flow rates (in g/10 min) of the PLA/MFC formulations achieved at 190 °C and with a weight of 2.16 kg

3.2 Control of the migration and associated with thermal and mechanical properties

The trends of the mass loss percentage as function of the square root time are reported for all formulations in *Figure 2*. It is interesting to observe how the formulations containing only the plasticizers showed a greater plasticizer loss over time than their counterparts containing MFC, confirming their ability in limiting the plasticizer migration. Specifically, OLA showed a greater tendency to migrate than PEG confirming the trends encountered during melt flow tests. The presence of the MFCs makes more impervious the plasticizer migration as also confirmed by the values of the calculated diffusion coefficients (using the second Fick's law [7]) that are reported in *Table 2*. The *D* values reported considered any eventual crystallization process which could have influenced the plasticizer migration, for this reason at day 1 and at day 50 crystallinity degree has been evaluated (also reported in *Figure 2*). Thermal results showed a general increment of crystallinity, but when the MFCs were added to the plasticized matrices, their effect resulted more marked thus significantly contributing to the plasticizer mass loss reduction. Also in this case, Exilva-MFCs showed a higher reduction of mass loss connected with a higher increase in crystallinity.

This concept is also evident from the variation of mechanical properties (tensile strength and elongation at break in MD to CD). The stress at break of the biocomposites grows over time in correlation to the loss of mass of the plasticizer; in parallel the elongation at break undergoes with an abrupt reduction for the plasticized matrices. The reduction in elongation at break over 50 days is less evident in biocomposites due to the ability of MFCs to retain the plasticiser in the mixture, thus preventing it from migrating to the surface and the film from losing its flexibility.

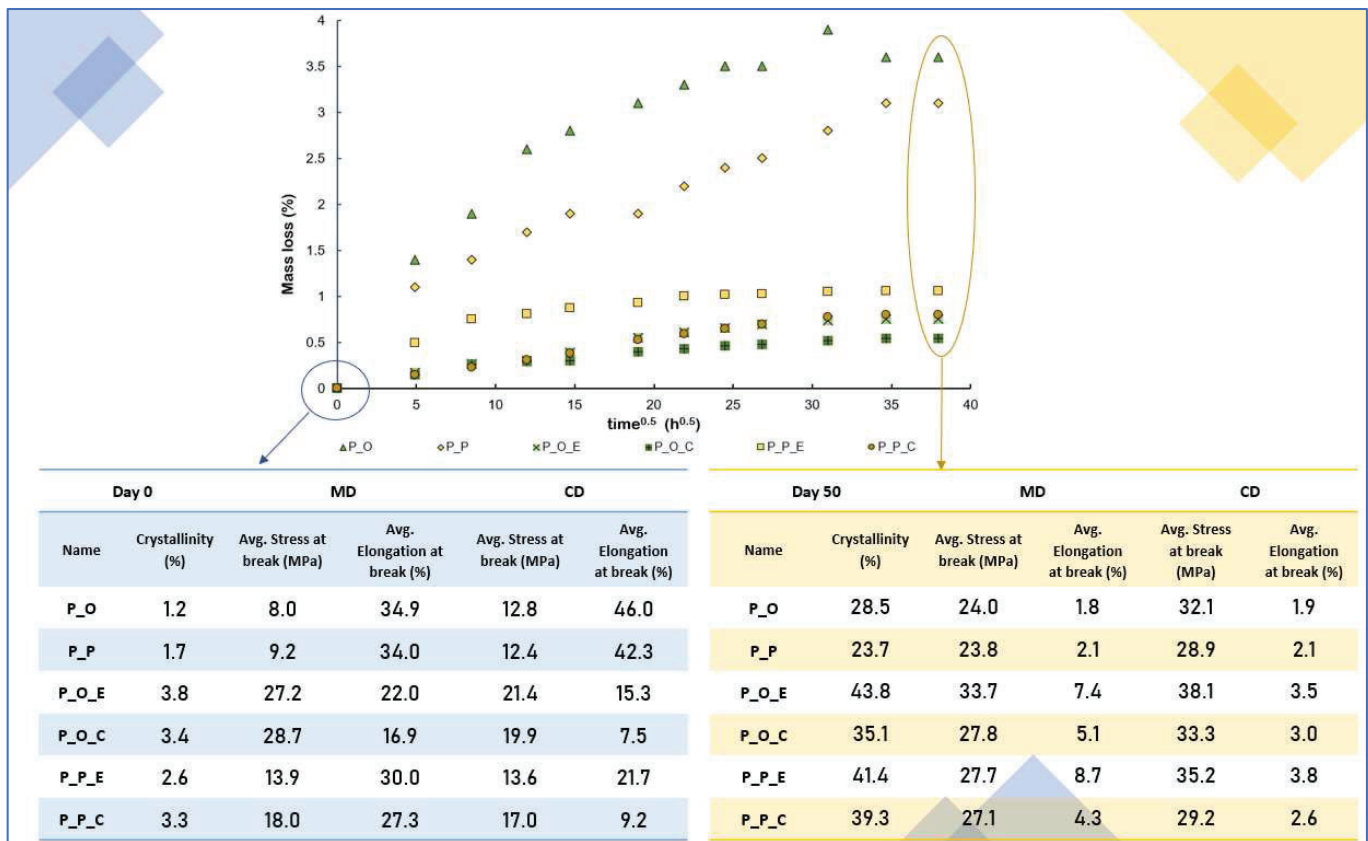


Figure 2. Trend of mass loss over time, showing how crystallinity and mechanical properties vary from day 0 to day 50 on calendered films

Table 2: Diffusion coefficients of biocomposites studied

Name	Diffusion coefficient (D) (cm ² /s)
P_O	$2.4 \cdot 10^{-10}$
P_P	$2.3 \cdot 10^{-10}$
P_O_E	$1.4 \cdot 10^{-10}$
P_O_C	$1.4 \cdot 10^{-10}$
P_P_E	$1.9 \cdot 10^{-10}$
P_P_C	$1.35 \cdot 10^{-10}$

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