Innovative Bio-based Poly(Lactic Acid)/Poly(Alkylene Furanoate)s Fiber Blends for Sustainable Textile Applications

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Abstract
This work aims at producing and investigating, for the first time, the microstructural and thermo-mechanical properties of fibers constituted by poly(lactic acid) (PLA)/poly(alkylene furanoate)s (PAFs) blends for textile applications. Two different PAFs have been investigated, i.e., poly(octylene furanoate) (P8F) and poly(dodecylene furanoate) (P12F), which have been blended with PLA in different concentrations and spun through a lab-made wet spinning device. The microstructural investigation of the fiber cross-section evidenced domains of PAFs homogeneously dispersed within the PLA matrix. The immiscibility of the produced blends was also suggested by the fact that the glass transition temperature of PLA was unaffected by the presence of PAF. The thermal stability of PLA was not substantially influenced by the PAF content, whereas the water absorption tendency decreased with an increase in P12F fraction. The mechanical properties of PLA/P8F blends decreased with the P8F amount, while for PLA/P12F fiber blends the stiffness and the strength were approximatively constant by increasing the P12F content. The drawing process, performed at 70 °C and with two different draw ratios, brought an interesting increase in the mechanical properties of PLA fibers upon P12F introduction. These promising results constitute the basis for future research on these innovative bio-based fibers.

Keywords Poly(lactic acid) · Furanoates · Fibers · Drawing · Mechanical properties

Introduction
It is well known that the problem of plastic pollution has recently attracted increasing scientific and popular concerns [1]. The public awareness of the environmental impact of fossil fuel-based polymers has steeply increased in the last years and has forced industries and governments to develop initiatives to move toward a more sustainable use of plastics [2]. Improving the sustainability of plastic products is thus a big challenge for human society, and an increasing number of bio-based matrices have been recently developed and industrialized [3–5]. Biopolymers, which are polymers that are biodegradable and/or produced starting from renewable resources, are a promising option for reducing the environmental impact of plastics [6]. In the last decades bio-derived, recyclable and compostable plastics have been extensively investigated, and bioplastics like poly(lactic acid) (PLA) [7], polyhydroxyalkanoates (PHAs) [8], and thermoplastic starch [9] were introduced on the market. In particular, PLA is a linear aliphatic poly(α-ester) [10], synthesized by the ionic polymerization of lactic acid [4], which is formed by the dehydration-condensation of two lactic acid molecules. Since the lactic acid molecules possess two different optical forms, labeled as L-lactic acid and D-lactic acid, lactide presents three different isomeric forms: L-lactide, D-lactide, and D,L-lactide (also known as meso lactide) depending on how the building blocks are linked together [11, 12]. From the ionic polymerization of lactide [4], which is formed by the dehydration-condensation of two lactic acid molecules. Since the lactic acid molecules possess two different optical forms, labeled as L-lactic acid and D-lactic acid, lactide presents three different isomeric forms: L-lactide, D-lactide, and D,L-lactide (also known as meso lactide) depending on how the building blocks are linked together [11, 12]. From the ionic polymerization of L-lactide and D-lactide, two different PLA are obtained, known as poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA), respectively [13, 14]. Commercially speaking, the most widely used PLA is composed of PLLA with a small content of PDLA [15]. On the other hand, from the polymerization of meso lactide,
the amorphous polymer known as poly (L, d-lactic acid) (PDLLA) can be obtained [16, 17]. PLA is a biopolymer exhibiting high tensile modulus (approximately 3 GPa), good mechanical strength (higher than 60 MPa), high workability, and higher transparency in comparison to other biopolymers, showing also a compostable and recyclable nature [7]. For all these reasons it has been intensively studied as a possible substitute for traditional matrices in composite materials and in packaging applications [18–20].

In recent years, a new family of biopolymers containing a furan ring structure derived from 2,5-furandicarboxylic acid (FDCA) has attracted the attention of researchers to produce homopolymers [21, 22] or copolymers [23]. However, due to the lack of an economical and viable industrial process for producing the precursors, furan-based polymers are not yet widely used [24]. Among the different types of furan polymers, poly(alkylene furanoate)s (PAFs) are the most widely investigated, since they possess interesting mechanical and thermal performance and significantly high barrier properties [25]. The most important PAF is probably poly(ethylene 2,5 furandicarboxylate) (PEF), the bioderived counterpart of polyethylene terephthalate (PET) [26]. PEF presents improved gas barrier properties in comparison to PET, good thermal and mechanical resistance, but it shows a brittle behavior at room temperature. Thanks to these properties, PEF could be a potential substitute for PET only if its brittleness will be significantly reduced. Besides PEF, different PAFs homopolymers based on aliphatic diols with a higher number of carbon atoms have been recently synthesized, like poly(propylene 2,5-furandicarboxylate) (PPF) [27], poly(butylene 2,5-furandicarboxylate) (PBF) [28], poly(hexamethylene 2,5-furandicarboxylate) (PHF) [29], poly(octylene 2,5-furandicarboxylate) (POF or P8F) [30], poly(decylene 2,5-furandicarboxylate) (PDeF) [31, 32] and poly(dodecylene 2,5-furandicarboxylate) (PD2F) [33]. An increase in the number of carbon atoms of the diol leads to a decrease of the thermo-mechanical properties, like the elastic modulus, the glass transition temperature ($T_g$) and the melting temperature ($T_m$) [34]. On the other hand, by increasing the alkyl chain length the resulting polymers will exhibit a more ductile behavior and they could be thus applied for packaging applications [35].

Therefore, blending bio-based plastics already present on the market with innovative biopolymers possessing tailor-made properties could represent a new opportunity to completely exploit their potential [36]. A polymer blend is a physical or mechanical mixture in which at least two polymers are combined, to produce a new material having different physical properties with respect to its constituents. Generally speaking, polymer blends can be broadly divided into three categories. In immiscible or heterogeneous polymer blends the constituents are present in separate phases. In a miscible or homogeneous polymer blend, the mixture of two or more polymers results in a single-phase structure [37, 38]. In a compatible polymer blend, the constituents are present in separate phases but the blend exhibits macroscopically uniform properties due to the strong interaction between the components of the polymer alloy. Although the majority of polymers are generally non-miscible, blending is a common technique to modify and/or improve the properties of polymer matrices, usually in a more cost-effective way in comparison to the synthesis of new plastics. Several works in the literature report the blending of PPAF with different biopolymers or petroleum-based polymers, such as poly(e-caprolactone) (PCL) [39], poly(propylene) (PP) [40], thermoplastic starch [41], poly (3-hydroxybutyrate) (PHB) [42, 43] and poly(butylene 2,5-furan dicarboxylate) (PBF) [44].

Some studies have been also recently conducted on PAFs based blends. Papageorgiou et al. [45] performed a comprehensive investigation on poly(alkylene furanoate)/poly(alkylene terephthalate) (PAT) blends and concluded that in many cases PAF/PAT blends were immiscible. PEF and PPF showed dynamic homogeneity and miscibility, while only PPF/PBF blends seemed to be partially miscible. As reported in the work of Pouloupolou et al. [46], also PEF/PBF mixtures were immiscible. Another paper concerning PLA/PBF blends has been performed by Long et al. [44]. Even these blends were immiscible, they possessed interesting optical properties. In another work of Long et al. [47], PLA/PBF blends with a PBF content of 5 wt% showed remarkable mechanical properties, with elongation at break values about 18 times higher than that of neat PLA and without substantially affecting the stiffness and the yield resistance. Moreover, PBF introduction was responsible for a remarkable increase in the gas barrier properties. In conclusion, Fredi et al. [48] studied the preparation of PLA/PAF blends in the form of cast films.

In the last years, the improvement of the sustainability of polymeric fibers represented a challenge both from an academic and industrial point of view. Fibers are either natural or man-made products that, by definition, forms the basic element of fabrics and other products such as vegetable tissues, mineral substances or textile products [49]. Nowadays fibers are widely applied in many fields, e.g. textiles, fabrics and composite materials. Due to the considerable employment of synthetic fibers, a more sustainable fiber production must be performed, involving also the use of bio-based polymers [50]. One of the most widely applied processes to improve the mechanical properties and the dimensional stability of the fibers is drawing. This process is often performed at elevated temperatures (i.e. between the $T_g$ and the $T_m$ of the matrix), in order to promote the mobility of the macromolecules and their alignment along the drawing direction. Generally speaking, the drawing process results
in an increased polymer chain density and an improved strength in comparison to the as-spun fibers [51].

On the basis of these considerations, this study reports the production through wet spinning process of PLA/P8F and PLA/P12F blends in the form of fibers which, to the best of the authors' knowledge, has never been investigated before in the open literature. The main goal of the work is to develop novel fully bio-based PLA/PAF fibers for textile applications with improved toughness and lower water absorption tendency compared to neat PLA, thereby tackling the main shortcomings of PLA. A complete characterization of the as-spun fibers was performed, in order to highlight the effect of the PAF type and content on the microstructural, thermal, and mechanical properties of the resulting blends. Fibers with optimized formulation were then drawn at different draw ratios, in order to detect the influence of the chain alignment and of the P12F addition on their physico-mechanical properties.

Materials and Methods

Materials

The PLA used in this work was an Ingeo® biopolymer 4032D (density = 1.24 g/cm³, MFI at 210 °C and 2.16 kg = 7 g/10 min) produced by NatureWorks LLC (Minnetonka, United States) in pellets form. Two different PAFs have been used for the production of fiber blends. The first is poly (1,8-octylene 2,5-furandicarboxylate) (P8F). It is a biopolymer derived from a two-steps polycondensation of 2,5-dimethylfuran-dicarboxylate (DMFD) and 1,8-octamethylene glycol, and as reported in the work of Papageorgiou et al. [33] it shows a $T_g$ of $-5$ °C and a $T_m$ of 111 °C. Both PAFs were synthesized in form of small slabs in the Department of Chemistry of the Aristotle University of Thessaloniki (Greece). Chloroform (HPLC grade), ethanol (purity 99.9%) and methanol (purity 99.9%) were purchased by Carlo Erba Reagents Srl (Milano, Italy). All the materials were used as received.

Samples Preparation

Fiber Spinning Process

As briefly explained in the introduction, fiber blends were prepared through a wet spinning process. Neat PLA, PLA/P8F, and PLA/P12F mixtures were dissolved in chloroform by the fact that this solvent has been reported to dissolve both PLA and furan-based polyesters with a relatively long alkyl chain [45, 52]. The polymer concentration was 0.75 g over 5 mL of solvent, and the resulting solution was magnetically stirred at 40 °C for approximately 3 h. The obtained solutions were then mildly ultrasonicated for 10 min in a Labsonic LBS1 bath (Falc Instruments Srl, Bergamo, Italy), in order to remove small air bubbles that were formed during the stirring process, and then transferred in a glass syringe with a capacity of 10 mL. The spinning process was performed with a lab-made device shown in Fig. 1. The glass syringe containing the polymer solution was fixed on a Harvard apparatus Model 11 Single Syringe 55–1199 (Harvard apparatus Inc., Holliston, USA) and connected with a 18 gauge needle, which was subsequently sealed to the non-solvent bath. After some preliminary trials, the spinning velocity has been set at 0.007 mL/min, while the speed of the take-up rollers was fixed at 60 rpm. The solution passed then through a non-solvent bath, with the aim of removing the solvent and produce thus continuous fibers. The non-solvent
bath contained 80 vol% of ethanol and 20 vol% of methanol, since both these solvents were able to induce PLA crystallization [53]. The obtained fibers were collected with take up rollers and left 24 h in the air, in order to allow complete solvent evaporation. The fibers were then stored in a desiccator with dry silica salts until their use.

Two different groups of fiber blends have been produced. The first was a PLA/P8F mixture with P8F weight concentrations from 5 to 30 wt%, while the second was a PLA/P12F blend with P12F contents from 5 to 30 wt%. Each sample was labeled as PLA_xPAF, where x represents the weight content of PAF in the polymer alloy. Neat PLA fibers were also spun for comparison. An attempt was made to spun neat P8F and P12F fibers, but it was successful only with the neat P12F ones. Table 1 reports the list of the produced fibers, together with the nominal weight fraction of PAF.

### Fiber Drawing

To improve the mechanical properties of the obtained fibers and to investigate the effect of the macromolecular orientation, a drawing process has been performed both on neat PLA and on the PLA_20P12F fiber blends. This composition was selected on the basis of the results of the mechanical characterization performed on the as-spun fibers (see Paragraph 3.1). The drawing process has been performed using an Instron® 5969 electromechanical testing machine (ITW Test & Measurement and Equipment, Norwood, USA), equipped with a 100 N load cell and an Instron® 3119-409 thermostatic chamber. Fibers having a gauge length of 50 mm were deformed at a fixed strain rate and under a constant temperature. In the work of Hyon et al. [54], the drawing of PLA fibers was performed at 160 °C and the highest strength and modulus were obtained when the as-spun fibers were drawn with a DR of 13. On the other hand, in the study of Hilborn et al. [55], as-spun fibers were subjected to a drawing process at 90 °C with DR ranging from 2 to 10, followed by a heat setting at 120 °C. In this work, a drawing temperature of 70 °C was utilized. This temperature was selected as it lays in the temperature window between the $T_g$ of PLA (approx. 55 °C) and the melting point of P12F, which starts at 80 °C (see DSC tests in Fig. 5). It is also important to underline that at 70 °C also P12F is above its $T_g$ (i.e. − 5 °C, as reported by Papageorgiou et al. [33]). In these conditions, the motion of the polymeric chains in both the blend constituents is favoured. Considering the deformation level of the fibers during the drawing process, it was possible to determine the DR, which is usually defined as the ratio between the collection ($R_c$) and the feeding ($R_f$) rate, as reported in Eq. (1) [56].

$$DR = \frac{R_c}{R_f} = \left(\frac{D_i}{D_f}\right)^2$$  \hspace{1cm} (1)

where the $D_i$ represents the initial fiber diameter, and $D_f$ represents the diameter of the fiber after the drawing process. In the works of Hyon et al. [54] and Hilborn et al. [55], high DR levels have been achieved, and the mechanical properties of the drawn fibers were thus noticeable enhanced. At the drawing temperature selected in the present work, it was not possible to reach these DR values, as the fibers were fractured before reaching the desired deformation. Therefore, in this paper, the total deformation of the fibers was set at 50% or 150%, applied at a drawing speed of 50 mm/min. These deformations respectively correspond to nominal DR levels of 1.7 and 2.7. Table 2 reports the list of the drawn fibers and the parameters involved in the drawing process.

### Experimental Techniques

Light microscope (LM) micrographs of the produced fiber blends were obtained with a CH-9435 Heerbrugg optical microscope (Heerbrugg, Switzerland). According to the experimental procedure developed by Fredi et al. [57], LM images of the fiber cross-section were obtained by winding

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**Table 1** List of prepared as-spun fibers

| PAF content [wt%] | PLA/P8F  | PLA/P12F |
|------------------|----------|----------|
| 0                | PLA      |         |
| 5                | PLA_5P8F | PLA_5P12F|
| 10               | PLA_10P8F| PLA_10P12F|
| 20               | PLA_20P8F| PLA_20P12F|
| 30               | PLA_30P8F| PLA_30P12F|
| 100              | –        | P12F     |

**Table 2** List of the prepared drawn fibers and parameters involved in the drawing process

| Sample                  | Nominal DR | Total deformation [%] | Drawing speed [mm/min] | P12F content [wt%] | Draining T [°C] |
|-------------------------|------------|-----------------------|------------------------|--------------------|-----------------|
| PLA_D1.7                | 1.7        | 50                    | 50                     | 0                  | 70              |
| PLA_20P12F_D1.7         | 1.7        | 50                    | 50                     | 20                 |                 |
| PLA_D2.7                | 2.7        | 150                   | 50                     | 0                  | 70              |
| PLA_20P12F_D2.7         | 2.7        | 150                   | 50                     | 0                  |                 |
the fibers to a poly(methyl methacrylate) (PMMA) parallelepiped and subsequently embedding the entire parallelepiped in cylindrical epoxy beads. The obtained epoxy beads were subsequently grinded with a sequence of abrasive papers of decreasing roughness (500, 800, 1200, 4000) and then polished with the help of polishing clothes with a roughness of 3 μm and 1 μm, in order to obtain smooth cross-section surfaces. Field Emission Scanning Electron Microscopy (FESEM) micrographs of the lateral surfaces of the fiber blends were obtained with a Zeiss Supra 60 (Carl Zeiss AG, Oberkochen, Germany) microscope after Pt–Pd sputtering, under an acceleration potential of 2.5 kV.

Differential scanning calorimetry (DSC) was performed with a Mettler DSC 30 calorimeter (Mettler Toledo, Inc., Columbus, USA) at 10 °C/min and between −50 and 250 °C, under a nitrogen flow of 100 mL/min. Specimens of approximately 6 mg were sealed in aluminum crucibles and subjected to a first heating scan, followed by a cooling scan, and a second heating scan. This analysis enabled the determination of the glass transition temperature \(T_g\), the melting temperature \(T_m\), the cold crystallization temperatures \(T_{cc}\), and the enthalpy values \(\Delta H_m\), \(\Delta H_{cc}\) of the blend constituents. The transition temperatures were measured with a precision of 0.02 °C, while the relative enthalpy values with a precision of 1% and an accuracy of 4%. Equation (2) shows how to evaluate the crystalline content \(\chi\) of the two polymer phases in the blends, expressed in [%].

\[
\chi = \frac{\Delta H_{m} - \Delta H_{cc}}{\Delta H_{m}^* \omega} \cdot 100
\]

where \(\Delta H_{cc}\) is the enthalpy of cold crystallization of PLA (or PAF) in the blend, \(\Delta H_m\) is the enthalpy of melting of PLA (or PAF) in the blend, \(\Delta H_{m}^*\) is the enthalpy of melting of fully crystalline PLA (or PAF), while \(\omega\) is the weight fraction of PLA (or PAF) in the blend. \(\Delta H_{m,PLA}^*\) value was equal to 93.7 J/g [58], while the evaluation of the crystalline content of P8F was not possible since the theoretical enthalpy of melting of P8F (\(\Delta H_{m,P8F}^*\)) has not been found in literature. \(\Delta H_{m,P12F}^*\) value was equal to 158.0 J/g [33].

Thermogravimetric analysis (TGA) was carried out with a Mettler TG50IR thermobalance (Mettler Toledo Inc., Columbus, USA). Specimens of approximately 4 mg were tested at a heating rate of 10 °C/min up to 700 °C, under a nitrogen flow of 100 mL/min. These tests allowed the establishment of the water loss \(m_{H_2O}\), of the degradation temperature \(T_d\), determined as the peak of the mass loss derivative (DTG) curve and representing the temperature at which the maximum degradation rate is achieved, and of the residual mass at 700 °C \(m_{700}\).

Quasi-static tensile tests were performed at room temperature by using an Instron® 5969 tensile testing machine (ITW Test & Measurement and Equipment, Norwood, USA) equipped with a 100 N load cell. Fiber specimens, having a gauge length of 50 mm, were mounted on paper frame supports and tested at a crosshead speed of 1 mm/min. At least six specimens were tested for each composition. In this way, the elastic modulus \(E\), the stress at yield \(\sigma_y\) and the failure properties of the fibers \(\sigma_b, \epsilon_b\) were determined.

**Results and Discussions**

**Characterization of the As-Spun Fibers**

Figure 2a–c show the cross-sections of the as-spun fiber blends obtained through light microscopy. It is possible to observe that all the fibers possess an elliptical cross-section without the presence of air bubbles. The scratches present on the fiber cross-section are caused by the grinding procedure. The non-circular cross-section of the as-spun fibers may be caused by the deformation imparted by the take-up rolls on the fibers emerging from the non-solvent bath, that still have solvent residues and are thus easily deformable. However, further studies are necessary to completely understand the mechanism behind this particular shape of the produced fibers.

The diameter of the fibers was measured from the LM images through the software ImageJ® (National Institutes of...
Neat PLA fibers are characterized by a mean diameter of 83 ± 10 μm, PLA_20P8F fibers have a mean size of 60 ± 7 μm, while the diameter of PLA_20P12F fibers is 89 ± 12 μm. Therefore, in both blends, the presence of PAF does not vary in a dramatic way the mean diameter of the spun fibers. Moreover, PAF domains homogeneously distributed within the PLA matrix can be detected. P8F domains in the center of the PLA matrix are characterized by a mean dimension of 3.6 ± 1.2 μm (Fig. 2b), while P12F domains in the center of the PLA matrix have a mean size of 3.0 ± 0.9 μm (Fig. 2c). From these micrographs, it is possible to infer that the produced fiber blends are immiscible. Furthermore, all PAF domains are mainly concentrated in the center of the fibers and their dimension decreases with the distance from the center of the fiber. A possible explanation is that both PAFs has a lower affinity to chloroform in comparison to, since PLA can be easily dissolved in chloroform, while only long alkyl chain PAFs can be dissolved in it [48]. Thus, during the first stage of the spinning process, the lateral surface of the fiber will be composed of PLA since it is more prone to coagulation in comparison to PAF and therefore PAF domains tend to aggregate in the chloroform-rich region (i.e. the center) of the fibers by the fact that they are less soluble in comparison to PLA. Furthermore, PAF domains tend to be concentrated in the center of the fiber by the fact that they act as filler inside the PLA matrix, and therefore, as reported in literature, the fillers in an extrusion process tend to be concentrated in the center of the fiber rather than in the outer surface [59, 60].

Figure 3a–c report FESEM micrographs of the lateral surfaces of neat PLA, PLA_30P8F, and PLA_30P12F fiber blends. The lateral surface of PLA fiber is smooth and does not present evident defects, while both PLA_30P8F and PLA_30P12F fibers show higher surface roughness together with small defects. Even from these micrographs, the elliptical cross-section of the fibers can be detected. A similar morphology for the PLA fibers has been reported also in the research of Hilborn et al. [55]. However, at a general level, it can be concluded that the produced fibers possess a rather good surface quality, and therefore they can be utilized for the subsequent characterization activities.

Figure 4 shows the DSC thermograms of as received P8F, neat PLA, and PLA_xP8F fiber blends (x = 5–30 wt%), while the most important results are listed in Table 3. P8F exhibits an endothermic melting peak at 143.8 °C, while the \( T_g \) can not be detected but it should be approximately − 5 °C, as reported in a previous paper by Bikiaris and colleagues on the thermal behavior of P8F [30]. PLA shows an endothermic melting peak at 166.2 °C and a \( T_g \) of 54.1 °C. It is interesting to observe that the \( T_g \) of PLA is unaltered by the presence of P8F, which confirms that PLA and P8F phases are immiscible. Another experimental evidence of the immiscibility of the blend resides in the well distinct melting phenomena of the two constituents. In Fig. 4b it is possible to observe the thermograms of the second heating scan. In comparison to the first heating stage, the peak related to the crystallization process of PLA is slightly decreased as the content of P8F increases. It is quite interesting to notice that the melting event related to the P8F phase, in the second heating scan, is characterized by a small shoulder at lower temperature. This shoulder might be related to the melting of a fraction of P8F characterized by a lower molecular weight. In the first heating scan (Fig. 4a) there is a small cold crystallization peak for the PLA phase, and the crystallinity content is about 27.2%, while in the second heating scan the cold crystallization peak is present, and its intensity is similar to that of the melting event. In conclusion, during the spinning process, the PLA within the blends is able to crystallize, while when the thermal history of the material is deleted upon a heating stage, PLA manifests a cold crystallization process leading to lower crystallization degrees in comparison to those calculated during the first heating scan, regardless of the presence of P8F.

Figure 5a, b show DSC thermograms of as received P12F, of neat PLA and P12F fibers, and their relative PLA_xP12F
fiber blends (x = 5–30 wt%), while the most important results are summarized in Table 4. P12F exhibits an endothermic melting peak at 105.3 °C, while the \( T_g \) can not be detected but it should be approximately − 5 °C, as previously shown by Papageorgiou et al. [33]. Moreover, it is interesting to notice that the thermograms of as received P12F and P12F fibers are quite similar, and this means that the wet spinning process performed did not alter the thermal properties of P12F. As in the case of PLA/P8F fiber blends, it can be observed that the \( T_g \) of PLA is unaltered by the presence of P12F, confirming thus that the produced fiber blends are immiscible. In the first heating scan (Fig. 5a) there is a small cold crystallization peak of PLA and the crystallinity content is approx. 27.2%, while in the second heating scan the cold crystallization peak is more evident. Furthermore, concerning P12F, during the cooling scan, a cold crystallization peak was measured and it is quite similar to the melting peak related to P12F, and therefore it is reasonable to state that the cold crystallization peak in the second heating scan is related only to PLA. It could be also interesting to understand how the crystallinity of PLA is affected by the introduction of P12F. Considering \( \chi_{PLA} \) values of the blends reported in Table 4, it is possible to notice that the crystallinity of the PLA phase progressively increases with the P12F concentration, passing from 27.2% of the neat PLA up to 34.9% for the PLA_30P12F fiber blend. It can be therefore concluded.

| Sample          | \( T_g \) PLA [°C] | \( T_m \) PLA [°C] | \( \Delta H_m \) PLA [J/g] | \( T_m \) P8F [°C] | \( \Delta H_m \) P8F [J/g] | \( T_{cc} \) PLA [°C] | \( \Delta H_{cc} \) PLA [J/g] | \( \chi_{PLA} \) [%] |
|-----------------|-------------------|-------------------|-----------------------------|-------------------|-----------------------------|------------------------|-----------------------------|-----------------|
| PLA             | 54.1              | 166.2             | 37.6                        | –                 | –                           | –                      | 96.5                        | 12.0            |
| PLA_5P8F        | 57.1              | 165.5             | 38.3                        | 140.3             | 2.5                         | 82.5                   | 9.7                         | 32.1            |
| PLA_10P8F       | 55.4              | 157.4             | 35.5                        | 139.9             | 8.2                         | 83.1                   | 8.9                         | 31.5            |
| PLA_20P8F       | 58.4              | 165.9             | 34.3                        | 138.7             | 15.5                        | 83.8                   | 8.3                         | 34.7            |
| PLA_30P8F       | 56.5              | 165.2             | 29.8                        | 140.5             | 24.2                        | 87.2                   | 10.8                        | 29.0            |
| P8F As Received | –                 | –                 | –                           | –                 | –                           | –                      | –                           | –               |
| PLA             | 56.1              | 163.1             | 44.0                        | –                 | –                           | –                      | 118.1                       | 39.9            |
| PLA_5P8F        | 56.5              | 166.2             | 34.9                        | 140.3             | 2.2                         | 105.1                  | 32.5                        | 2.7             |
| PLA_10P8F       | 57.3              | 166.8             | 32.7                        | 139.3             | 4.2                         | 104.3                  | 32.4                        | 0.4             |
| PLA_20P8F       | 56.4              | 167.0             | 32.1                        | 139.4             | 8.2                         | 102.5                  | 31.8                        | 0.4             |
| PLA_30P8F       | 56.2              | 166.8             | 25.9                        | 140.1             | 11.2                        | 106.8                  | 25.7                        | 0.3             |
| P8F As Received | –                 | –                 | –                           | –                 | –                           | –                      | –                           | –               |

Table 3 Results of DSC tests on PLA_xP8F fiber blends (x = 5–30 wt%)

\( T_g \) PLA glass transition temperature of PLA; \( T_m \) PLA melting temperature of PLA; \( \Delta H_m \) PLA melting enthalpy of PLA; \( T_m \) P8F melting temperature of P8F; \( \Delta H_m \) P8F melting enthalpy of P8F; \( T_{cc} \) PLA cold crystallization temperature of PLA; \( \Delta H_{cc} \) PLA cold crystallization enthalpy of PLA; \( \chi_{PLA} \) crystallinity content of PLA.
that P12F domains within the PLA matrix play a nucleating effect, improving thus the crystallinity content. From the $T_{c,PLA}$ results reported in Table 4, it can be also noticed that the crystallization temperature of PLA is decreased upon the P12F introduction. In the first heating scan, it can be seen that $T_c$ values of PLA phase pass from 96.5 °C up to 83.3 °C with a P12F content of 30 wt%, and a similar trend can be seen also in the second heating scan. This result confirms the nucleating effect played by P12F domains within the PLA matrix. However, further analyses will be necessary in the future to have a better comprehension of the crystallization behaviour of PLA in these blends.

Figure 6 shows the TGA thermograms and DTG curves of both PLA_xP8F (Fig. 6a, b) and PLA_xP12F (Fig. 6c, d) fiber blends (x = 5–30 wt%), while the most important results are collected in Table 5. In both PLA_xP8F and PLA_xP12F thermograms (Fig. 6a, c) it is possible to notice a mass loss starting from approximately 100 °C. This mass loss is certainly linked to the evaporation of the water absorbed by the blends. In the case of PLA_xP8F samples, the addition of P8F does not lower the water absorption tendency of PLA. On the other hand, as it is possible to notice in Fig. 6c, as the content of P12F increases in the PLA_xP12F fiber blends, the step related to water loss tends to decrease, which suggests that the addition of P12F in the blends helps in reducing the water absorption tendency of PLA. All the samples lose the majority of their mass between 300 °C and 400 °C. PLA_xP8F fiber blends show the DTG peak linked to PLA at approximately 370 °C, while the peak associated with the P8F phase is approximately at 408 °C. P12F presents the steepest degradation step among all the tested fiber blends. As reported in the work of Bikiaris et al. [61], the thermal stability of both P8F and P12F is similar to that of PEF, PPF, and PHF but slightly higher than that of PBF. In conclusion, it is possible to notice from the data reported in Table 5 that the thermal stability of PLA is not substantially affected by the presence of both P8F and P12F. Furthermore, the $m_{700}$ values tend to increase by increasing the PAF content in the blends, and they are systematically higher for PLA/P12F blends in comparison to PLA/P8F ones.

Figure 7a, b show representative stress–strain curves of neat PLA and the relative PLA_xP8F (Fig. 7a) and PLA_xP12F fiber blends (Fig. 7b). Furthermore, the most important results are collected in Table 6. The stress–strain curves reported in Fig. 7a, b possess a rather low signal-to-noise ratio, since the load cell selected was characterized by high sensitivity and therefore the local environmental noise was also detected. Nevertheless, the low signal-to-noise ratio did not dramatically affect the quality of the obtained results. As expected, PLA fibers show a quite high modulus (2.2 GPa) and interesting failure properties ($\sigma_b = 30.1$ MPa, $\epsilon_b = 127%$) [62]. On the other hand, the mechanical properties of PLA_xP8F fibers tend to decrease by increasing the content of P8F. At elevated P8F concentrations (30 wt%), the ductility of the fiber is completely lost since $\epsilon_b$ decreases to 1.6%, and also $\sigma_b$ of the fiber drops down to 7.2 MPa. The cause of the observed decrease in the mechanical properties may be the low interfacial adhesion between P8F domains and PLA matrix, especially at elevated P8F amounts. In the work of Jompang et al. [63], PLA and poly(butylene succinate) (PBS) fiber blends were prepared through melt spinning,

Fig. 5 DSC thermograms of P12F as received, P12F fiber, PLA fiber, and PLA_xP12F fiber blends (x = 5–30 wt%). a First heating scan, b second heating scan.
Table 4 Results of DSC tests on PLA_xP12F fiber blends (x = 5–30 wt%)

| Sample          | $T_g_{P12F}$ [°C] | $T_g_{PLA}$ [°C] | $T_m_{PLA}$ [°C] | $\Delta H_m_{PLA}$ [J/g] | $T_m_{P12F}$ [°C] | $\Delta H_m_{P12F}$ [J/g] | $T_{cc \_PLA}$ [°C] | $\Delta H_{cc \_PLA}$ [J/g] | $\chi_{PLA}$ [%] | $\chi_{P12F}$ [%] |
|-----------------|-------------------|------------------|------------------|--------------------------|-------------------|--------------------------|---------------------|--------------------------|----------------|----------------|
| **First heating scan** |                   |                   |                   |                          |                   |                          |                     |                          |                 |                 |
| PLA             | –                 | 54.1              | 166.2             | 37.6                     | –                 | –                        | 96.5                | 12.0                     | 27.2           | –               |
| PLA_5P12F       | –                 | 55.5              | 165.3             | 38.3                     | 102.2             | 1.7                      | 69.1                | 14.2                     | 27.1           | 1.1             |
| PLA_10P12F      | –                 | 55.8              | 157.3             | 36.6                     | 100.2             | 3.0                      | 79.2                | 11.7                     | 29.5           | 1.9             |
| PLA_20P12F      | –                 | 54.4              | 165.4             | 30.9                     | 100.9             | 8.3                      | 83.9                | 7.3                      | 31.5           | 5.2             |
| PLA_30P12F      | –                 | 54.6              | 165.1             | 26.9                     | 101.4             | 11.6                     | 83.3                | 4.0                      | 34.9           | 7.3             |
| P12F            | –                 | –                 | –                 | –                        | –                 | –                        | –                   | –                        | –              | –               |
| P12F_As Received| –                 | –                 | –                 | –                        | 102.9             | 69.1                     | –                   | –                        | –              | 43.8            |
| **Second heating scan** |                   |                   |                   |                          |                   |                          |                     |                          |                 |                 |
| PLA             | –                 | 56.1              | 163.1             | 44.0                     | –                 | –                        | 118.1               | 39.9                     | 4.4            | –               |
| PLA_5P12F       | –                 | 56.9              | 154.3             | 40.2                     | –                 | –                        | 102.5               | 38.6                     | 1.8            | –               |
| PLA_10P12F      | –                 | 54.7              | 164.8             | 39.3                     | 97.7              | 1.0                      | 107.7               | 38.5                     | 0.9            | 6.3             |
| PLA_20P12F      | –                 | 54.5              | 154.1             | 32.6                     | 100.1             | 5.6                      | 103.1               | 30.3                     | 3.1            | 17.7            |
| PLA_30P12F      | –                 | 56.3              | 155.7             | 31.8                     | 101.1             | 7.4                      | 104.5               | 24.3                     | 11.4           | 15.6            |
| P12F            | –18.4             | –                 | –                 | –                        | 103.2             | 61.3                     | –                   | –                        | –              | 38.8            |
| P12F_As Received| –11.7             | –                 | –                 | –                        | 103.1             | 56.8                     | –                   | –                        | –              | 35.9            |

$T_g_{P12F}$ glass transition temperature of P12F; $T_g_{PLA}$ glass transition temperature of PLA; $T_m_{PLA}$ melting temperature of PLA; $\Delta H_m_{PLA}$ melting enthalpy of PLA; $T_m_{P12F}$ melting temperature of P12F; $\Delta H_m_{P12F}$ melting enthalpy of P12F; $T_{cc \_PLA}$ cold crystallization temperature of PLA; $\Delta H_{cc \_PLA}$ cold crystallization enthalpy of PLA; $\chi_{PLA}$ and $\chi_{P12F}$ crystallinity content of PLA and P12F, respectively.
and they reported a decrease in the mechanical properties as the content of PBS was increased. Also in that work the observed drop was attributed to the low adhesion between PBS and the PLA matrix. On the other hand, the values of $E$, $\sigma_y$, and $\sigma_b$ of the PLA$_x$P12F blends (Fig. 7b) are approximately constant by increasing P12F content (and in some cases also slightly enhanced), while the $\epsilon_b$ is decreased. However, the observed decrease in the failure strain is not dramatic, neither at elevated P12F amounts. It is also interesting to notice that neat P12F fibers were not broken during the tensile tests, since the maximum elongation achievable with the utilized testing equipment has been reached. In particular, PLA$_{30}$P12F sample has an elastic modulus of 2.2 GPa and a stress at break of 32 MPa. Even if P12F possesses an extremely high ductility ($\epsilon_b > 240\%$), the failure strain of this blend decreases to 46%. The relatively low ductility of PLA/P12F fiber blends may be correlated to relatively poor adhesion between the P12F domains and PLA matrix. One of the strategies to improve the adhesion between two polymer phases, which was extensively studied in literature [64], is to use compatibilizers, such as maleic anhydride-functionalized polymers, to enhance the affinity between the two phases. It could be also possible to work on the production of PLA/PFAs blends with small amount of different nanofillers,
such as nanosilica, nanocellulose, or carbon nanotubes, in order to improve the affinity between the constituents and reducing the size of the dispersed polymer phase (i.e. the minority component).

**Characterization of the Drawn Fibers**

According to the results obtained through the mechanical characterization of the as-spun fibers, the most promising ones were the PLA/P12F blends, because even at relatively high P12F contents the stiffness and the stress at break of the neat PLA were not negatively affected (and in some cases also slightly improved), while the observed elongation at break was not dramatically decreased. Knowing that both the microstructural features and the mechanical properties of the fibers could be strongly affected by the drawing process, it was decided to prepare neat PLA and PLA_20P12F drawn fibers at two different DR levels. Figure 8a, b report the LM micrographs of the cross-section of the fibers drawn applying a DR equal to 2.7. As already seen in the case of the as-spun fibers (see Fig. 2), also drawn fibers possess an elliptical cross-section, but with a less pronounced eccentricity. The mean diameter of PLA_D2.7 fibers is 41 ± 2 μm (− 43% with respect to the as-spun PLA fibers), while the diameter of PLA_20P12F_D2.7 fibers is 53 ± 3 μm (− 43% with respect to the as-spun PLA_20P12F fiber blends). Moreover, from Fig. 8b it is evident that the diameter of P12F domains within the PLA matrix decreases from 3.0 ± 0.9 μm up to 1.7 ± 0.7 μm (− 43%). The overall decrease in the mean diameter of the fibers and also the drop in the diameter of P12F domains within the PLA matrix is a direct consequence of the drawing process.

Figure 9 reports a comparison between the stress–strain curves of the PLA and PLA_20P12F fibers, before and after the drawing process, while the most important results are summarized in Table 7. As it could be expected, the drawing process performed at 70 °C noticeably improves the mechanical properties of the fibers, regardless of the presence of P12F in the samples. As expected, the increase of the applied DR produces a systematic enhancement of all the mechanical properties of the fibers. Blend containing 20 wt% of P12F and drawn with a nominal DR of 1.7 and 2.7 show an improvement of $E$ by 24% and 76%, of

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### Table 5 Results of the TGA tests of the PLA_xP8F and PLA_xP12F fiber blends (x = 5—30 wt%)

| Sample       | $m_{H_2O}$ [%] | $T_d$ [°C] | $m_{700}$ [%] |
|--------------|----------------|------------|---------------|
| PLA          | 3.1            | 373.7      | 0.49          |
| PLA_5P8F     | 3.7            | 378.3      | 0.53          |
| PLA_10P8F    | 3.9            | 377.3      | 0.81          |
| PLA_20P8F    | 3.8            | 377.7      | 0.62          |
| PLA_30P8F    | 3.8            | 374.7      | 1.51          |
| PLA          | 3.1            | 373.7      | 0.49          |
| PLA_5P12F    | 2.2            | 370.8      | 0.79          |
| PLA_10P12F   | 2.5            | 379.3      | 0.57          |
| PLA_20P12F   | 2.2            | 377.2      | 1.13          |
| PLA_30P12F   | 1.9            | 372.7      | 2.27          |
| P12F         | 0.6            | 408.3      | 1.81          |

$m_{H_2O}$ water loss; $T_d$ degradation temperature; $m_{700}$ residual mass at 700 °C.
by 78% and 194%, and of $\sigma_b$ by 195% and 13%, respectively, in comparison to the as-spun PLA_20P12F fibers.

Neat PLA fibers drawn with a nominal DR of 1.7 and 2.7 have an increase of $E$ by 77% and 127%, of $\sigma_y$ by 227% and 326%, and a decrease of $\sigma_b$ by 42% and 69%, respectively, with respect to the as-spun PLA fibers. As expected, the fibers drawn with a nominal DR of 2.7 reported enhanced mechanical properties and lower $\sigma_b$ in comparison to the fibers drawn with a nominal DR of 1.7. This is caused by the fact that higher DR means a higher orientation of the macromolecules and therefore improved mechanical properties, as reported in several publications [65, 66]. It could be hypothesized that the observed increase of the elastic modulus and of the stress at break upon the drawing process could be related to an increase of the crystallinity of the constituents. However, it was not possible to test the drawn fibers through DSC tests, because of the low amount of available material, and XRD tests were not able to elucidate these aspects in a satisfactory way. Further tests will be needed to explain the observed trend. Considering the effect of the P12F on the mechanical properties of the drawn fibers, it can be observed that the stiffness and the stress at break values of the PLA_20P12F are not so far from those of the neat PLA fibers, at both DR levels. Interesting and unexpected results were instead obtained considering failure strain data. The elongation at break of the PLA_20P12F fiber blends dramatically increases by increasing the nominal DR, and $\epsilon_b$ values are considerably higher than those of neat PLA fibers. The peculiar behavior concerning the elongation at break has been already observed for several amorphous polymers [67] and blends [68]. The observed increase in the elongation at break values of the drawn fiber blends may be linked to the fact that the drawing process performed at 70 °C might have improved the adhesion between P12F domains and PLA matrix, and therefore, during the application of a tensile load, a better load distribution on the P12F domains can be realized. Since neat P12F fiber reports an extremely high elongation at break (see Table 6), the overall elongation at break of the fiber blends tends to significantly increase if the load distribution is performed more efficiently. Another possible explanation for the observed increase of the elongation at break can be found in the paper of La Mantia et al. [68] on polyethylene (PE)/polyamide 6 (PA6) blends. In that work

### Table 6 Results of tensile tests on the PLA_xP8F and PLA_xP12F fiber blends (x = 5–30 wt%)

| Sample   | $E$ [GPa] | $\sigma_y$ [MPa] | $\sigma_b$ [MPa] | $\epsilon_b$ [%] |
|----------|-----------|------------------|------------------|-----------------|
| PLA      | 2.2 ± 0.4 | 30.6 ± 3.9       | 30.1 ± 4.1       | 127 ± 48        |
| PLA_5P8F | 1.9 ± 0.3 | 17.6 ± 4.4       | 17.0 ± 4.6       | 101 ± 31        |
| PLA_10P8F| 2.0 ± 0.4 | 14.9 ± 2.0       | 15.6 ± 3.2       | 88 ± 45         |
| PLA_20P8F| 1.4 ± 0.3 | 12.4 ± 3.8       | 14.3 ± 3.5       | 56 ± 22         |
| PLA_30P8F| 1.5 ± 0.9 | 5.1 ± 3.2        | 7.2 ± 5.2        | 1.6 ± 1.0       |
| PLA      | 2.2 ± 0.4 | 30.6 ± 3.9       | 30.1 ± 4.1       | 127 ± 48        |
| PLA_5P12F| 2.2 ± 0.4 | 26.5 ± 6.4       | 25.0 ± 4.2       | 28 ± 10         |
| PLA_10P12F| 1.8 ± 0.4 | 25.2 ± 5.1       | 25.0 ± 3.2       | 43 ± 14         |
| PLA_20P12F| 2.5 ± 0.6 | 35.2 ± 8.4       | 36.5 ± 8.4       | 76 ± 26         |
| PLA_30P12F| 2.2 ± 0.5 | 33.8 ± 7.6       | 31.9 ± 5.4       | 46 ± 13         |
| P12F     | 0.2 ± 0.1 | 8.6 ± 0.5        | -                | > 240           |

$E$: elastic modulus; $\sigma_y$: yield stress; $\sigma_b$: stress at break; $\epsilon_b$: strain at break.

### Table 7 Results of tensile tests on the drawn fibers

| Sample         | $E$ [GPa] | $\sigma_b$ [MPa] | $\epsilon_b$ [%] |
|----------------|-----------|------------------|-----------------|
| PLA_D1.7       | 3.9 ± 0.1 | 98.7 ± 4.3       | 74 ± 23         |
| PLA_20P12F_D1.7| 3.1 ± 0.6 | 65.0 ± 2.9       | 224 ± 59        |
| PLA_D2.7       | 5.1 ± 1.1 | 128.2 ± 15.7     | 39 ± 18         |
| PLA_20P12F_D2.7| 4.4 ± 0.2 | 107.3 ± 22.5     | 86 ± 29         |

$\sigma_b$: by 78% and 194%, and of $\epsilon_b$ by 195% and 13%, respectively, in comparison to the as-spun PLA_20P12F fibers.

**Fig. 8** Light microscope images of the polished cross-section of the drawn fibers (the contour of the fibers was highlighted in red for better clarity). a PLA_D2.7, b PLA_20P12F_D2.7

**Fig. 9** Comparison between the stress–strain curves of the as-spun and drawn PLA and PLA_20P12F fibers.
it was shown that these two polymers were immiscible, and during the application of a tensile load, the PA6 domains acted as defects, worsening thus of the mechanical properties of the blends. After the drawing process, the PA6 domains inside the matrix were elongated and oriented in the same direction. In these conditions, the worsening effect provided by the PA6 domains was mitigated [68]. Regarding PLA/P12F fiber blends prepared in this work, it is possible to hypothesize that during the drawing process, P12F domains have been elongated toward the drawing direction. In fact, from the LM images reported in Fig. 8b it is possible to notice that the mean diameter of the P12F domains within drawn fibers is significantly decreased. Consequently, the defect-like nature of the P12F domains is mitigated, and the elongation at break values considerably improved.

In conclusion, by comparing PLA and PLA_20P12F drawn fibers, it is possible to state that P12F introduction helps in improving the ductility of the PLA fibers, if properly drawn, without substantially impairing their stiffness and stress at break values. Further improvements could be obtained in the future by an optimization of the drawing conditions. The prepared fibers blends could be therefore interesting for the development of novel sustainable textiles with improved mechanical features.

Conclusions

The present work investigated for the first time the microstructural, thermal and mechanical properties of novel bio-based fiber blends, constituted by PLA and two furan based matrices, i.e., poly(1,12-dodecylene 2,5-furandicarboxylate) (P12F) and poly(1,8-octylene 2,5-furandicarboxylate) (P8F), produced through wet spinning process. The microstructural characterization performed on the as-spun fibers evidenced that both PLA/P8F and PLA/P12F fiber blends were immiscible, with PAF domains homogeneously dispersed within the PLA matrix. DSC analysis highlighted that the degree of crystallinity of both PLA and P12F phases tended to increase with the P12F content. TGA analysis showed that the thermal stability of PLA was practically unaltered by the presence of either P8F or P12F. Besides, P12F helped to decrease the water absorption tendency of PLA. Tensile tests evidenced a steep decrease in the mechanical properties by increasing the P8F content for PLA_xP8F fiber blends, probably correlated to the low adhesion between the P8F domains and the PLA matrix. On the other hand, PLA_xP12F fiber blends reported mechanical properties comparable to that of neat PLA fibers, without a dramatic drop of the failure strain.

Microstructural analysis on the drawn fibers showed that the mean diameter of the P12F domains within the PLA matrix decreased by 43% with respect to the as-spun fibers. Tensile tests evidenced that both the elastic modulus and the stress at break of PLA_20P12F drawn fibers were slightly lower in comparison to PLA drawn fibers. On the other hand, the strain at break of PLA_20P12F drawn fibers increased by 303% and 220% compared to PLA fibers when the nominal DR was of 1.7 and 2.7, respectively. The improvement in the strain at break of the fiber blends upon the drawing process was probably correlated to a progressive deformation of P12F domains along the strain direction, promoting a better adhesion between the P12F domains and the PLA matrix. In conclusion, the addition of P12F to PLA has been proven to be very successful in improving the strain at break of the produced fibers after the drawing process, without significantly decreasing the stiffness and the strength of the PLA fibers. This study contributed to improving the knowledge about bioderived furan-based polymers and the relative blends with PLA, and elucidated also the effect of the drawing process on the microstructural and mechanical features of the prepared fibers. According to the obtained results, these fibers could be a good candidate for the replacement of polyester fibers traditionally applied in textile or packaging sector.

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Data Availability Data and materials are available under requests.

Declarations

Conflict of 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.

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