PLA/BIOPA BIOBLENDS FOR FDM: MECHANICAL AND FRACTURE BEHAVIOUR

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ABSTRACT

The fracture behaviour of PLA/PA bioblends has been investigated in order to extend its processing through fused deposition modeling printing by pellets supply (FDM-p). The viability of the processing technique in creating in situ microfibrillated composites (MFCs) through the microfibrillation of the PA dispersed phase has been evaluated as a way to strengthen and toughen PLA. The mechanical behaviour was assessed through uniaxial tensile tests performed at room temperature (22°C) using type 1BA dumbbell tensile test specimens (ISO527-2) featuring an unidirectional infill pattern fully oriented in the longitudinal direction of the samples. The fracture behaviour was assessed through the determination of the CTOD value just before the crack propagation onset in single-edge-notched tension (SENT) test geometry featuring a multi-axial multilayer infill pattern. For all the samples, a nominal filling density of 100 % was predefined. Morphological observations revealed that the 3D printing conditions used in this study allowed the manufacturing of in-situ MFCs with an average diameter of the PA microfibrils as low as 320 nm. The developed morphology led to a significant increase in the structural integrity of the parts manufactured through FDM-p, as clearly evidenced by the 206% increase in the CTOD values as compared to samples obtained through conventional compression-moulding using the same raw pellets.

KEYWORDS: PLA, Bioblends, Bio-PA, CTOD, Fused deposition modeling

1. INTRODUCTION

Melt blending Poly(Lactic Acid) (PLA) with other polymers is considered as the most practical and economic strategy to improve its properties and industrial applicability. Among the numbers of second polymer phase combinations, melt compounding PLA with biobased Polyamides (BioPA) has gained an increasing interest in the last years despite the well reported immiscible character between both polymers [1–4]. As for any immiscible polymer blend, the main challenges are focused on both their “compatibilization” and the control of the resulting morphology because both contribute in the effectiveness of local stress transfer between phases during mechanical loading.
In this context, Li et al. reported that the creation of a fibrillar morphology in polypropylene/poly(ethylene terephthalate) blend, suitably compatibilized and oriented during final part’s manufacturing, could increase the fracture toughness, particularly during crack propagation [5]. This type of polymer blends has been referred to as in-situ microfibrillated composites (MFCs). Regarding PLA/BioPA blends, Kakroodi et al. concluded that the generation of these in-situ MFCs has a great potential to enhance PLA crystallization and its mechanical properties [2].

However, manufacturing MFCs involves at least a three-step process: 1) the melt blending of both polymers using a twin screw extruder, 2) the manufacturing of pellets with a precursor morphology (by single or twin screw extruder) and finally 3) the processing of the final part. Nevertheless, it is well known that PLA is highly sensitive to thermo-oxidative degradations during processing at high temperatures. Due to this chemical instability, the control of the final morphology in PLA-based blends is complex because the break up stage of the fibrillar phase could be easily reached due to the meniscal instability. Therefore, a mixed morphology consisting of drops and fibrils below their critical reinforcement length is usually obtained, decreasing the potential reinforcement effect [6].

The inherent processing characteristic of the Fused Deposition Modeling (FDM) printing with pellets supply can take advantage of the MFC technology avoiding at least two processing stages during piece manufacturing. As it is well known, parts manufactured through FDM suffer from poor mechanical properties and low surface quality, as compared to injection molded items. Both of them are controlled by the adhesion quality of the different filaments and the global porosity of the part obtained. Thus, a controlled fibrillar morphology can contribute to mitigate this concern.

The present communication aims at presenting the most relevant results in terms of mechanical behavior and structural integrity regarding the use of PLA/BioPA bioblends for the manufacturing of in situ MFC parts through FDM.

2. MATERIALS AND METHODS

2.1. Materials

A commercially available PLA grade (Ingeo PLA4032D, D-lactic content = 2%, MFI (210°C,2.16kg) = 6.4 ± 0.3 g/10 min, ρ(25°C) = 1.24 g.cm−3) was purchased from Natureworks LLC (Arendonk, Belgium). A styrene-acrylic multifunctional-epoxide oligomeric agent (referred to as SAmfE), namely Joncryl-ADR -4400F®, was kindly supplied by BASF (Ludwigshafen, Germany) with an epoxy equivalent weight of 485 g.mol−1 and a functionality of about 14. The predominantly bio-based PA10.10 (ρ (25°C) = 1.05 g.cm−3) was kindly supplied by Dupont (Midland, USA) under the trade name Zytel RS LC1000 BK385.

2.2. Processing and bioblends manufacturing

In the present study, the above mentioned low thermal stability of PLA at high temperatures was counteracted through reactive extrusion. Pre-dried PLA pellets were melt blended with 0.5 wt.% of SAmfE following the procedure and conditions previously reported in [4]. The manufactured material was referred to as PLAREx.

A two-step process was used to manufacture PLAREx/PA parts through DFM. Initially, PLAREx pellets were melt compounded with 30 wt.% of PA using a co-rotating twin-screw extruder with a screw diameter of 25 mm (L/D=36) (Kneter 25X24D, Collin GmbH, Ebersberg, Germany). More information regarding the processing conditions and experimental procedure can be found in [6]. The unstretched extrudate was water-cooled and pelletized. Prior to the different processing steps, all the materials were dried at 80 °C for 4h in a Fiovan hopper-dryer (dew point =−40°C).

Finally, 3D printing of type 1BA dumbbell tensile test specimens (ISO527-2) and single-edge-notched tension (SENT) test geometry was performed using a Voladora NX-pellets printer (Tumaker, Oyarzun, Spain) from the obtained pellets. The pattern used for the printing was 2 shells and the infill nominal density was set to 100%. Dumbbell specimens were printed using a rectilinear infill pattern fully oriented in the longitudinal direction of the samples in order to evaluate the effect of the morphology on the mechanical properties. SENT samples were printed using a multi-axial multilayer infill pattern. The printing speed was 1260 mm/min, resulting in an apparent shear rate of approximately 210 s−1 in the nozzle exit (nozzle diameter 0.8 mm). The nozzle temperature was set to 220 °C and the bed temperature to 110 °C. Prior to printing, pellets were vacuum dried at 80 °C for 4 hours. For comparison purposes, PLAREx was printed following the same procedure.

In the present work, results obtained on the 3D printed parts were compared to solid samples. For this purpose, both PLAREx and PLAREx/PA pellets were compression moulded into 0.6 mm thick plates in a hot plate press (IQAP LAP PL-15, IQAP Masterbatch SL, Barcelona, Spain) for 3 min at 220 °C under 40 MPa. Since both melt processes induced a different thermal history to the manufactured parts, an annealing procedure was performed on all the samples at 110 °C for 2h30.

2.3. Morphology observation

Scanning electron microscopy (SEM, JEOL, JSM-7000IF, Japan) observations were carried out at 2 kV on the cryogenically fractured surface of the compression moulded and 3D printed PLAREx/PA samples. Prior to
observation, sample surfaces were sputter coated with a thin platinum-palladium layer. The cryofractured surfaces of PLAREx/PA samples have been equally etched in order to highlight the dispersion of the PA phase. For this purpose, fractured samples were immersed in a water-methanol solution (1:2 by volume) containing 0.025 mol.L⁻¹ of NaOH for 6 days at 23°C.

2.4. Tensile testing

The uniaxial tensile behavior was assessed according to ISO 527 using a universal testing machine (Sun 2500, Galdabini, Cardano al Campo, Italy) equipped with a 5 kN load cell and type IBA dumbbell specimens. Deformations were measured using a video extensometer (OS-65D CCD, Minstron, Taiwan). All experiments were performed at room temperature (RT). The Young’s Modulus (E), the yield strength (σy), the strain at yield (εy) and the strain at break (εb) were determined from the engineering stress-strain curves. All reported values are averages of 5 valid specimens tested at a crosshead speed of 10 mm.min⁻¹ whereas E was determined at 1 mm.min⁻¹.

2.5. Fracture characterization

The fracture analysis was carried out by determining the crack tip opening displacement (CTOD) at the onset of crack propagation. SENT specimens features the following nominal dimensions: Length L= 65 mm, width W=15 mm, thickness t=2 mm (3D printed) and t= 0.6 mm (compression moulded) and distance between grips ZG=45 mm. The initial crack (a) was sharpened using a fresh razor blade with an edge radius of 0.13 µm. In order to perform a preliminary inspection of a possible change in the fracture behavior, a unique ligament length equal to 7.5 mm was tested (a/W=0.5). Uniaxial tests were performed at RT on a servo-hydraulic testing system (Amslet HC25, Zwick Roell, Ulm, Germany), equipped with a 25 kN load cell at a crosshead speed of 1 mm.min⁻¹. A video monitoring system (two digital cameras Xenoplan 1.4/23-0.902, Schneider Kreuznach, Germany) coupled to an optical strain measurement system (ARAMIS®, GOM GmbH, Germany) was used to determine the CTOD value just before the crack propagation onset. The interested reader can find more information regarding the parameters used for the digital image correlation analysis in [7].

3. RESULTS AND DISCUSSION

3.1. Morphological analysis

Since the final part properties are highly dependent on the induced morphology during processing, SEM observations were carried out on the cryogenically fractured surface of the 70/30 PLAREx/PA blends manufactured through compression moulding and 3D printing, respectively. As shown in Figure 1.a and 1.b, the cryofractured surface morphology of the PLAREx/PA items manufactured through both melt-processing did not display any clear evidence of phase-separated domains. The cryo-induced fracture did not induce voiding nor phase particle debonding, suggesting a proper interfacial adhesion between both polymers. Similar morphological observations have already been reported by [8,9] for PLA/PA blends manufactured through reactive processing. Authors ascribed these observations to a synergetic effect between a possible reactive compatibilization together with a decrease in the interfacial energy between both polymers during melt-blending, thus enhancing the interfacial adhesion. Such behaviour is essential to provide efficient load transfer from the PLA matrix to the PA disperse phase during mechanical loading.

![Figure 1. SEM micrographs of the cryofractured surface of PLAREx/PA blends manufactured through compression moulding and 3D printing before (a and b) and after (c and d) the selective surface etching process. In figure b and d, the arrow indicates the printing direction. Scale bare = 2 µm.](image-url)

Since the real dispersion of the PA phase into the PLAREx-based bioblends was not clearly revealed on the previous cryo-fractured surfaces, selective surface etching of the PLAREx matrix was performed. Figure 1.c and 1.d show the dispersion of the remaining PA phase after the selective PLAREx surface etching procedure. Regarding PLAREx/PA bioblends manufactured through compression moulding, it can be seen that submicronic near-spherical droplets coexist with elongated PA domains. Significant morphological changes occurred with the modification of the processing technique. Regarding PLAREx/PA bioblends manufactured through 3D printing, the high shear rate applied at the nozzle exit enabled a successful stretching of the PA phase into fine microfibrillar structures which seem to be homogeneously dispersed and fully oriented in the printing direction. The average diameter of the PA microfibrils was as low as 320 nm. The microfibrils also seem to have very high aspect ratios. However, it was not...
possible to measure the aspect ratio of the individual microfibrils because of their excessive length.

3.2. Tensile properties

Typical tensile engineering stress-strain curves are shown in Figure 2 and the tensile properties are summarized in Table 1. Compression moulded PLA_3E samples exhibited a local maximum in the engineering stress-strain curve associated with a yield point. Nevertheless, the formation of crazes prevented the propagation of a stable neck, resulting in a brittle fracture. According to Table 1, it is interesting to note that PLA_3E 3D printed samples exhibited similar E, σ_y, and ε_y values that the compression moulded ones taking into account the standard deviations. Upon yielding, the numerous thin PLA filaments (0.75 cm of diameter) which are fully oriented in the load direction allowed to reduce the overall triaxial stress state generated under tensile loading, thus leading to a 50% increase in the strain at break as compared to compression moulded samples.

![Figure 2. Typical tensile engineering stress-strain curves for compression moulded and 3D printed samples.](image)

As expected, the addition of 30 wt.% of PA led to a decrease in the stiffness and strength from 3.5 to 2.4 GPa and from 70 to 55 MPa for the compression moulded samples. Regarding the failure strain, a brittle behavior was equally observed for these samples due to the unstable necking of the tensile specimens. This was ascribed to the irregular microstructure featuring large PA domains, leading to premature failure. Interestingly, these results were found when studying the tensile behavior of PLA_3E/PA bioblends manufactured through 3D printing. Hence, PLA_3E/PA samples exhibited a ductile behavior wherein a yield point is clearly observed in the engineering stress-strain curve, followed by the propagation of a stable neck up to 100% of deformation (c.f. Table 1). It can be observed that the elastic modulus and the yield stress of 3D printed samples increased up to 9% and 16 %, respectively, as compared to compression moulded specimens. Since all samples exhibited a similar Xc (c.f. Table 1), such increase in stiffness and strength can be attributed to the reinforcement effect provided by the creation of numerous and regular microfibrils mainly oriented in the load direction. This observation equally suggested that the microfibrils length is above the critical fibre length to achieve reinforcement. Upon yielding, the presence of the abovementioned microstructure together with a proper adhesion between both phases (c.f. Figure 2) greatly enhanced the toughness of the 3D printed samples.

According to the above, since 3D printed dumbbell specimens can be compared to a unidirectional composite material, the elastic modulus values are likely to be predicted using micromechanics (i.e. mixing rule). In this context, it was considered that the fibre length was greater than the critical fibre length of PLA (93.6 J.g⁻¹) (Hakim et al. (2017)).

### Table 1. Uniaxial tensile properties at 10 mm.min⁻¹ (E at 1 mm.min⁻¹)

<table>
<thead>
<tr>
<th>Processing</th>
<th>Compression Moulding</th>
<th>3D printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>PA</td>
<td>PLA_3E</td>
</tr>
<tr>
<td>E (MPa)</td>
<td>1.5 ± 0.1</td>
<td>3.5 ± 0.2</td>
</tr>
<tr>
<td>σ_y (MPa)</td>
<td>46 ± 1</td>
<td>70 ± 2</td>
</tr>
<tr>
<td>ε_y (%)</td>
<td>18 ± 1</td>
<td>2.36 ± 0.09</td>
</tr>
<tr>
<td>σ_b (%)</td>
<td>155 ± 27</td>
<td>2.7 ± 0.1</td>
</tr>
<tr>
<td>Xc (%)a</td>
<td>41 ± 6</td>
<td>42 ± 7</td>
</tr>
</tbody>
</table>

a The tested specimens were cut from the annealed tensile samples. The degree of crystallinity, Xc, was determined from the first DSC heating runs at 10 °C.min⁻¹, as follows Xc = DHm/DHm0*100. Where DHm is the melting enthalpy and DHm0 the melting enthalpy for a 100% crystalline PLA (93.6 J.g⁻¹) (Hakim et al. (2017))

b not determined

According to the above, since 3D printed dumbbell specimens can be compared to a unidirectional composite material, the elastic modulus values are likely to be predicted using micromechanics (i.e. mixing rule). In this context, it was considered that the fibre length was greater than the critical reinforcement length and that a good adhesion was achieved between both phases. Under isostress conditions, calculations allow to determine that E= 2.42 GPa, while under isotrain conditions, E= 2.83 GPa. These results are in line with the experimental results compiled in Table 1 and confirmed that 3D printed PLA_3E/PA samples tend to behave as long fibre-reinforced composite materials featuring continuous unidirectional fibers mainly oriented in the load direction.

3.3. Fracture behaviour

After verifying the creation of a microfibrillar morphology in the samples manufactured through 3D printing, the structural integrity was evaluated. In this context, a preliminary inspection of the possible change in the fracture toughness was evaluated through the
determination of the CTOD at the onset of crack propagation. For this purpose, SENT specimens were prepared with a multidirectional filling pattern, as previously described in section 2.2.

Due to the shell (outfill region) that is required for manufacturing parts through FDM, in the crack propagation analysis, it was necessary to consider how far to extend the sharpening of the notch. After analyzing different options, it was decided to extend this sharpening so that it exceeds the shell region. The reproducible results between specimens led authors to consider this configuration as the most representative of the propagation process in the structure given the filamentary texture of the 3D printed part.

Figure 3.a shows a series of representative curves recorded during the test for the materials and processes obtained. For comparison purposes, authors chose to represent the Nominal engineering stress ($\sigma$) vs. the relative displacement of the analyzed region normalized by the actual ligament length (after notch sharpening) of the sample. Regardless of the type of processing, it can be seen that PLAREx samples exhibited a brittle behaviour, while PLA/PA bioblends exhibited a ductile behaviour, which one was much more pronounced for 3D printed samples. Figure 3.b shows the visual aspect of all the samples after testing at 1 mm.min$^{-1}$.

Table 2 compiles the values obtained after the DIC analysis. Regardless of the processing technique, adding 30 wt.% of PA to PLA clearly increased the CTOD values. That is, the value increased by 44% and 206% for compression moulded samples and 3D printed samples, respectively. This observation suggested that the PA phase is acting as reinforcement.

When the processing technique is considered, it can be observed that no significant differences were observed in the CTOD values between both PLAREx samples when the standard deviations are taken into account. In the present case and contrary to the behaviour observed through uniaxial testing tests for the 3D printed PLAREx samples, the reduced triaxial stress state induced by the numerous thin filaments was not sufficient to modify the inherent PLA brittleness. In contrary, 3D printed PLAREx/PA bioblends registered an increase of 139% in the CTOD values as compared to compression moulded specimens. Even though compression moulded samples are thinner (lower triaxiality), the behaviour observed for 3D printed PLAREx/PA samples can be principally attributed to the PA microfibrillar morphology which is acting as reinforcement, hence enhancing fracture toughness.

Table 2. Mean values of the parameters obtained after DIC analysis of SENT tests.

<table>
<thead>
<tr>
<th>Processing</th>
<th>Compression moulding</th>
<th>3D printing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLAREx</td>
<td>PLAREx/PA</td>
<td></td>
</tr>
<tr>
<td>CTOD (mm)</td>
<td>0.16 ± 0.02</td>
<td>0.18 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>± ±</td>
<td>± ±</td>
</tr>
<tr>
<td>Stress at CTOD (MPa)</td>
<td>53.9 ± 4.1</td>
<td>28.2 ± 4.9</td>
</tr>
<tr>
<td></td>
<td>± ±</td>
<td>± ±</td>
</tr>
<tr>
<td>Gc-App (KJ.m$^{-2}$)</td>
<td>15.3 ± 6.7</td>
<td>19.2 ± 4.5</td>
</tr>
<tr>
<td></td>
<td>± ±</td>
<td>± ±</td>
</tr>
<tr>
<td></td>
<td>22.5 ± 2.1</td>
<td>46.2 ± 9.9</td>
</tr>
</tbody>
</table>

In Figure 3.a, the stress level at which the crack started to propagate, stress at CTOD, is indicated by a dot for each material. The corresponding values were equally compiled in table 1. As can be seen, compression moulded PLAREx/PA samples exhibited higher stress levels than 3D printed ones. However, given the large experimental error reported, no clear conclusion can be highlighted considering this parameter.
In an attempt to obtain a numerical parameter that considered the stress combined with the CTOD value at the crack propagation onset, the analytical relationship proposed by Rivlin and Thomas (1953) was applied. According to these authors, the Critical Strain Energy Release Rate ($G_c$) for catastrophic fracture of rubbers in the presence of cracks (where the relationship proposed by Griffith is not satisfied) can be calculated for any relation of extension ($\lambda$) and crack length ($a$) from:

$$G(a, \lambda) = 2aK(\lambda)W_{UT}(\lambda)$$ (1)

Where $W_{UT}$ is the elastic energy stored by the material which in our case is considered to be reached when observing crack propagation, as the latter occurs in the elastic region. Based on experimental work the factor K has been defined as follows [10]:

$$K(\lambda) \cong 3/\sqrt{\lambda}$$ (2)

Considering this parameter (and its dispersion), the trends observed for the CTOD values are confirmed, although with a more conservative increase after the addition of PA (approximately 100%).

4. CONCLUSIONS

In this study, a rheologically modified PLA was melt blended with 30 wt.% of PA in order to successfully manufacture, in a second step, in situ-microfibrillated composites through a 3D fused deposition modeling process. Morphological observations revealed a proper interfacial adhesion between both polymers since no particle debonding was observed during the cryo-induced fracture. The high shear rate applied at the nozzle exit allowed the formation of long PA microfibrils, with a diameter as low as 320 nm, mainly oriented in the printing direction. Mechanical and fracture characterization revealed that adding 30 wt.% of PA to PLA promoted an increase in the structural integrity of the manufactured parts. That is, the microfibrillated PA phase acted as reinforcement, as clearly evidenced by the 206% increase in the CTOD value as compared to samples obtained through conventional compression-moulding. Finally, it can be affirmed that the FDM processing technique can be a useful tool for manufacturing in situ PLA/PA MFC parts with enhanced mechanical performances.

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