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Self-reinforced biobased composites based on high stiffness PLA yarns

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Abstract. In self-reinforced polymer composites (SRPC) the same polymer material forms both the reinforcing fibre and the matrix phase. The current project aims to develop a biobased alternative for these composites using polylactic acid (PLA). Both the development of the reinforcing fibres, the modelling and production of the composites are being studied. The stiffness of the PLA filaments could be increased to 9 GPa by optimising processing parameters during extrusion. After consolidation to composites, promising results are obtained showing that the stiffness of the PLA SRPC can match the requirements of currently used commercial self-reinforced polypropylene composites (ca 4GPa).

1. Introduction

There is a worldwide increasing demand for replacing fossil-based with biobased raw materials for the production of polymers, leading to a significant growth of bioplastics in terms of technological developments. However, there are still some drawbacks which prevent their wider commercialization in many applications. This is mainly due to their low mechanical performance and durability when compared to conventional polymers. Enhancement of these properties remains a significant challenge for biobased polymers. Therefore, there is a need to develop biobased, sustainable polymeric materials with high stiffness, high impact and high durability without impairing recyclability and at a similar price level of non-biobased solutions.

The development of self-reinforced polymer composites (SRPC) is proposed as a means to enhance the mechanical performance of biobased polymers. In such SRPCs the same polymer material forms both the fibre reinforcing and the matrix phase. These materials use a highly-drawn polymer fibre to reinforce a matrix of the same polymer family. SRPCs offer many advantages compared to standard fibre reinforced composites such as: lightweight, high specific stiffness and strength, high impact resistance, excellent fibre-matrix adhesion, inherent thermoformability and a good recyclability thanks to the mono material composite. These materials have a high potential for a variety of applications like house appliances, automotive parts with a need of a high impact resistance, body armours or sports equipment.

Fossil-based SRPCs, mainly polypropylene based, are already available on the market. A biobased alternative, however, does not yet exist. Among biobased polymers, polylactic acid (PLA) is an ideal material for the preparation of SRPC, as it can be produced with controlled molecular configuration (molecular weight, molecular alignment, crystallinity, ratio between L- and D-lactic acid etc.), resulting in a wide range of mechanical and thermal properties, including different melting points.

The above described demand for high performance biobased materials is exactly the challenge being tackled within the H2020 project BIO4SELF which aims at fully biobased SRPCs. To produce such biobased SRPCs two PLA grades are combined: a low melting temperature (Tm) one to form the matrix and an ultra-high stiffness and high Tm one to form the reinforcing fibres. It was chosen to combine the low and high Tm PLA by producing hybrid yarns consisting of low Tm matrix fibres and high Tm reinforcement fibres. The latter remain intact during further processing at a temperature above the melting temperature of the low Tm PLA but below the one of the high Tm PLA, resulting in a fully biobased composite material (see Figure 1).

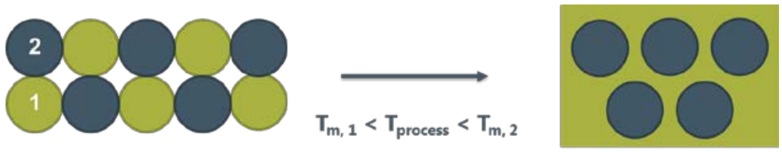

Figure 1. Production of self-reinforced composite (1: low Tm PLA, 2: high Tm PLA).

To successfully realise the BIO4SELF challenges, the complete value chain has to be actively involved. The consortium set-up within the project covers all required expertise and equipment going from the production of functionalised materials, over the melt spinning, finally resulting in composite end products. The current paper mainly focuses on the development of high stiffness PLA filaments and the modelling and production of simplified composite parts.

2. Description of materials and experimental procedure

2.1. Production of PLA filaments and yarns

The high Tm PLA material (with a Melt Flow Index of 10 g/10min at 190 °C) was purchased from Total-Corbion-PLA. The low Tm PLA material (with a Melt Flow Index of 15 g/10 min at 210 °C) was purchased from NatureWorks. At lab scale we used a multifilament extruder from Busschaert Engineering (named Spinmaster) at a throughput of 4 kg/hour. The extruder temperature was set at 240 °C. A yarn consisting of 48 filaments and a total titer of 240 dtex was produced. At industrial scale, we used a multifilament extruder in Svit (VÚCHV a.s) at a throughput of 18 kg/hour. The temperature was set at 245°C. A yarn consisting of 100 filaments and a total titer of 340 dtex was produced.

The high and low Tm PLA multifilaments, with a ratio 1:1, were then commingled in order to obtain a hybrid yarn consisting of both PLA grades.

2.2. Consolidation to composites

Unidirectional PLA composites were manufactured by winding the commingled yarns on a metal frame. The winding was dried overnight under vacuum chamber at 35˚C and then press consolidated in a two-step process. First, the material is heated to 165˚C under vacuum for 10 min. The heating is applied by the contact of two metal plates and controlled by two thermocouples. During heating, the low Tm PLA filaments are melted to form the matrix. Then, the winding is rapidly moved to the second section, where a pressure of 2 MPa is applied, and cooled down to 30˚C for 1 minute. The produced composite plates have dimensions of 400 x 250 x 2 mm.

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2.3. Mechanical characterization of composites

In order to determine the mechanical properties of the composites, the manufactured composites were tensile tested at different reinforcing filaments orientation, i.e. different high Tm PLA multifilaments orientation. Specimens for tensile tests, with dimensions of 180 x 20 mm, were cut from the manufactured unidirectional PLA composite plates. The specimens were cut at a range of angles to the winding direction (θ= 0˚, 15˚, 45˚, 90˚). Four specimens were prepared for each reinforcing filaments orientation. The static tensile tests were performed in an Instron tensile testing machine with a load cell of 25 kN. The cross-head speed was 10 mm/min. The strain was measured by two extensometers centred and aligned on each side of a specimen. The stiffness was determined in the strain range from 0.05 to 0.25 %.

To verify that the high Tm PLA multifilaments do not melt during the press consolidation, the measured values of composite stiffness, for θ= 0˚, were compared to theoretical predictions using the rule of mixture:

$$E_c = V_f E_f + (1 - V_f) E_m \tag{1}$$

where E_c is the composite stiffness, V_f is the volume fraction of high Tm PLA multifilaments, E_f is the stiffness of the reinforcing filaments, i.e. the stiffness of the high Tm PLA multifilaments, and E_m is the stiffness of the matrix, i.e. the stiffness of the low Tm PLA filaments.

The composite stiffness of composites tested at an angle θ, is predicted by [1]:

$$\frac{1}{E_\theta} = \left[\frac{1}{E_{11}}\right]\cos^4\theta + \left[\frac{1}{G_{12}} - 2\frac{v_{12}}{E_{11}}\right]\cos^2\theta\sin^2\theta + \left[\frac{1}{E_{22}}\right]\sin^4\theta \tag{2}$$

where E_θ is the composite stiffness, θ is the orientation of the reinforcing filaments, i.e. the high Tm PLA multifilaments, v_{12} is the major Poisson ratio, E_{11} is the composite stiffness for θ=0˚, E_{22} is the composite stiffness for θ=90˚, G_{12} is the shear modulus. The direction 1 refers to the winding direction and direction 2 refers to the perpendicular direction to the winding direction.

3. Results

3.1. Optimisation of the stiffness of PLA filaments

The mechanical performance of the PLA SRPC will mainly depend on the performance of the high Tm reinforcement fibres. Therefore, the challenge for the high Tm filament extrusion is to produce filaments with a maximum stiffness. Parameters investigated during the multifilament extrusion process were the influence of the capillary length over diameter ratio (L/D ratio) of the spinneret, the cold draw ratio and the comparison of a one- and two-step extrusion process.

When the extrusion and drawing was performed in one step, it was found that a high L/D ratio was beneficial for the filament's stiffness, going from 7.7 GPa for an L/D ratio of 2 to 8.7 GPa for an L/D ratio of 4. In addition, also a high cold draw ratio (up to 6 times drawing) resulted in a higher stiffness (Table 1). In general, the multifilaments, with a titer of 5 dpf (dtex per filament), reached a stiffness of approx. 9 GPa.

Table 1. Effect of L/D ratio and cold draw ratio on modulus of PLA yarn.

L/D ratio spinneret (-)	Cold draw ratio (x)	Modulus (GPa)
2	6.1	7.7
2.6	6.1	7.3
4	6.1	8.7
4	3.2	7.8
4	1.8	7.2

Next to the one-step process, also a two-step was investigated in which the extrusion was performed in a first step (at high take-up speed, 3000 m/min) followed by a separate drawing step (at 700 m/min). This also benefits the development of high stiffness PLA yarns. After successful parameterization at Centexbel, the extrusion process was upscaled at industrial scale by the company Fibrochem. This confirmed the advantages of a two-step versus a one-step process, resulting in a higher Young's Modulus (see Figure 2).

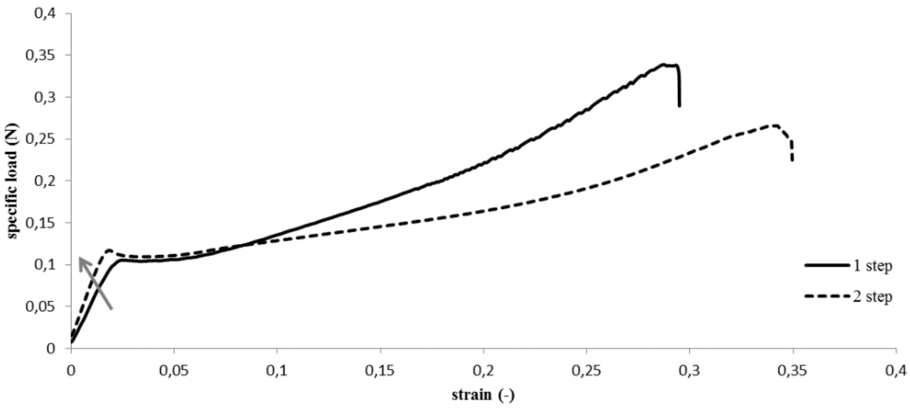

Figure 2. 1-step versus 2-step multifilament extrusion, arrow indicates increase in modulus.

Table 2. Filament properties produced with different spin finish.

	Oil based spin finish		Water based spin finish	
Properties	PLA high Tm	PLA low Tm	PLA high Tm	PLA low Tm
Stiffness [GPa]	7.6 ± 0.3	3.5 ± 0.1	7.5 ± 0.2	3.6 ± 0.1
Strength at break [MPa]	412 ± 67	66 ± 3	329 ± 51	28 ± 5

During multifilament extrusion, a spin finish needs to be applied on the yarn to regulate the friction among the filaments and the filament and the machine parts. That way, the built-up of electrostatic charges on the filament surface is prevented. In order to determine the effect of spin finish on the composite performance, composites were manufactured using multifilaments with two different spin finishes: an oil based one and a water based one. High and low melting temperature PLA multifilaments were produced with the two different spin finishes. As shown in Table 2, the strength at break is clearly influenced by the type of spin finish.

3.2. Consolidation to composites and the effect of spin finish on composite performance

In a composite material, the interphase region between the reinforcing filaments and the matrix material is crucial for the mechanical performance of the final composite. Some adhesion between the two constituents is required in order to obtain good composite mechanical properties. In a self-reinforced composite material one could argue that as the two constituents, the fibres and the matrix, are made of the same material, the adhesion between them should be strong. However, as spin finish is not specifically designed to promote adhesion between the reinforcing filaments and the matrix material, the presence of spin finish at the surface of the filaments might affect the fibre/matrix adhesion in a negative way.

The results of the static tensile testing are presented in Figure 3 and Figure 4. The composites are named “Oil” or “Water” depending on the spin finish used.

Regarding the composite stiffness, there are no large differences in the results obtained for the two types of composites “Oil” and “Water” for any θ angle. The experimental results obtained for $\theta = 0^\circ$ were compared to the theoretical estimation obtained with the rule of mixture (Equation (1)) and were found to be in good agreement assuming a 50% fibre volume fraction. The theoretical prediction was made using the filament properties presented in Table 1 and the composite stiffness is equal to 5.6 GPa. Equation (2) was used to predict the composite stiffness obtained for the composite tested at different angles. The Poisson’s ratio was set to 0.25 and the shear modulus was adjusted to best fit the experimental results obtained at 15° and 45°. For the “Oil” composite the shear modulus was set to 1.3 GPa and for the “Water” composite it was set to 1.4 GPa. It can be seen on Figure 3 that the experimental stiffness obtained for the composites for $\theta = 15^\circ$ is clearly above the theoretical curves. This may be due to the sample preparation, where specimens with a lower filament angle could have been cut out. The stiffnesses obtained at 45° are located on the theoretical curves. In conclusion, it is not possible to detect any effect of the spin finish on the composite stiffness. This is in line with the results reported by Alcock et al., where it was demonstrated that the interface properties do not influence the composite stiffness [1].

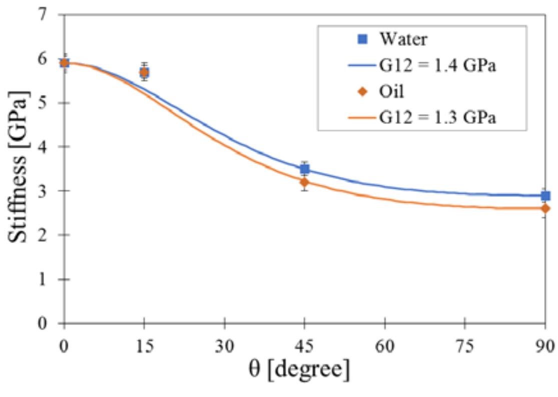

Figure 3. Stiffness of PLA composites tested at different loading directions.

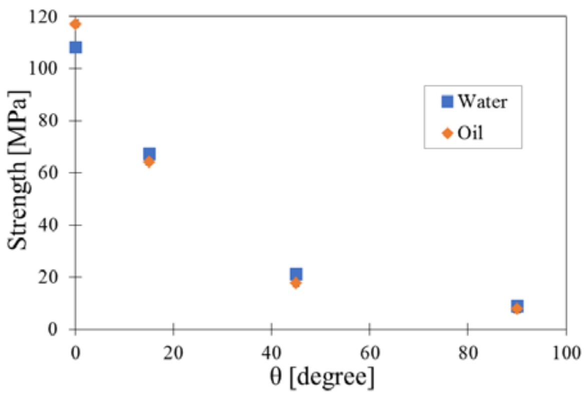

Figure 4. Strength of PLA composites tested at different loading directions.

Regarding the composite strength, similar conclusions can be drawn. All the results obtained are close to each other, except for the composite tested at $\theta = 0^\circ$. The strength values for the “Oil” composites are slightly higher than the “Water” composites. This is probably due to the difference in post yield response of the PLA_{HM} multifilaments. Spin finish has an effect on the manufacturing of the PLA filaments, which will result in filaments with different properties. Figure 5 and 6 show the stress-strain curve of the composite tested at $\theta = 0^\circ$, where it is possible to see the different behaviour around the yield region. Based on these results it is not possible to observe any effect of the different type of spin finish on the composite strength properties.

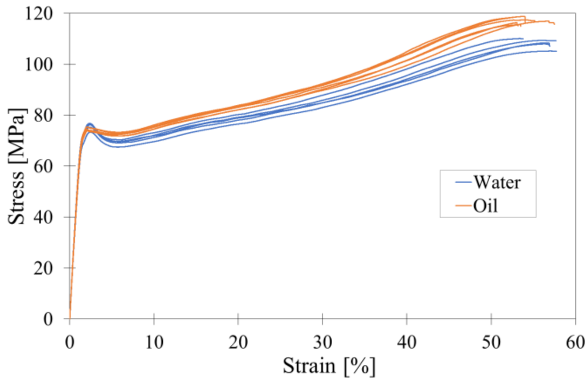

Figure 5. Stress-strain curve of the composite test for θ=0˚.

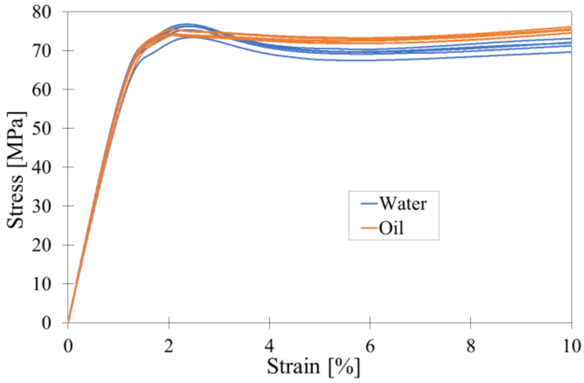

Figure 6. Detail view of the yield area of the stress-strain curve of the composite test for θ=0˚.

In conclusion, no effect of the spin finish type on the composite performance was observed. The oil based spin finish was however selected, as PLA is sensitive to water and an oil based spin finish tends to result in higher mechanical properties of the PLA yarns.
Next to the production of unidirectional composites, the commingled yarns produced with the oil based spin finish were processed into a woven fabric which was consolidated to a bidirectional composite plate. Promising results were obtained that show that the stiffness of the PLA composite can match the requirements of currently used commercial self-reinforced polypropylene (ca 4GPa).
As a next step, prototype composite parts for automotive and home appliances will be produced as demonstrators to illustrate the much broader range of industrial applications, e.g. furniture, construction and sports goods.

4. Conclusions and outlook

The results show that high stiffness PLA filaments can be produced on the standard multifilament extrusion equipment. These filaments were subsequently combined with low Tm PLA filaments into a hybrid yarn after which unidirectional and bidirectional SRPCs were manufactured. The effect of spin finish, needed to produce and process the multifilaments, on the composite properties was shown to be small. Overall composites with good mechanical performance, comparable to the current fossil based SRPCs, were obtained.
We will work on further optimisation of the PLA yarns, towards higher temperature resistance and higher stiffness e.g. by improvement of the 2-step process and the application of an additional heatsetting step. Future investigations will also include studying the adhesion between PLA filaments without any spin finish.

Acknowledgments
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[1] B. Alcock, N.O. Cabrera, N.-M. Barkoula, J. Loos, T. Peijs, “The mechanical properties of unidirectional all-polypropylene composites”, Composites: Part A 37 (2006) 716–726