High-stiffness PLA yarns for bio-based self-reinforced composites

Given the current demand for bio-based solutions, the aim of the project is to produce bio-based self-reinforced composites from polylactic acid (PLA). However, this requires the development of high-stiffness hydrolytically stable yarns. By stabilizing the PLA material and adjusting the extrusion parameters, yarns with stiffness of up to almost 9 GPa could be obtained.

Lien Van der Schueren, Guy Buyle
Centexbel, Ghent/Belgium
Bibiana Bizubova
Chemosvit Fibrochem, a.s., Svit/Slovakia

Bio-based composites

There is a worldwide increasing demand for replacing fossil-based with bio-based 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 bio-based polymers. Therefore, there is a need to develop bio-based, sustainable polymeric materials with high stiffness, high impact and high durability without impairing recyclability and at a similar price level of non-bio-based solutions.

Self-reinforced composites

The development of self-reinforced polymer composites (SRPC) is proposed as a means to enhance the mechanical performance of bio-based polymers. In such SRPCs the same polymer material forms both the fiber reinforcing and the matrix phase. These materials use a highly-drawn polymer fiber to reinforce a matrix of the same polymer family. SRPCs offer many advantages (Fig. 1) compared to standard fiber reinforced composites such as: lightweight, high specific stiffness and strength, high impact resistance, very good fiber-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 household appliances, automotive parts with a need of a high impact resistance, body armor or sports equipment.

Identified need: bio-based self-reinforced composites

Fossil-based SRPCs, mainly polypropylene-based, are already available on the market. A bio-based alternative, however, does not yet exist. Among bio-based polymers, PLA is an

Fig. 1
Advantages of self-reinforced composites
(Courtesy of project partner ITA)

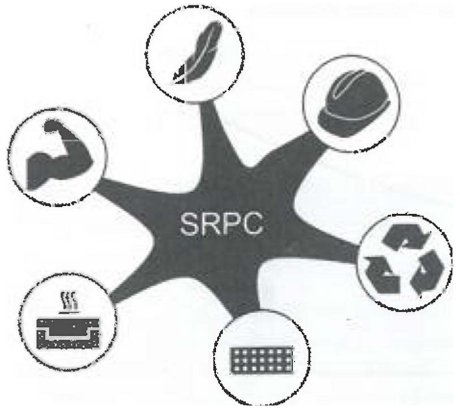
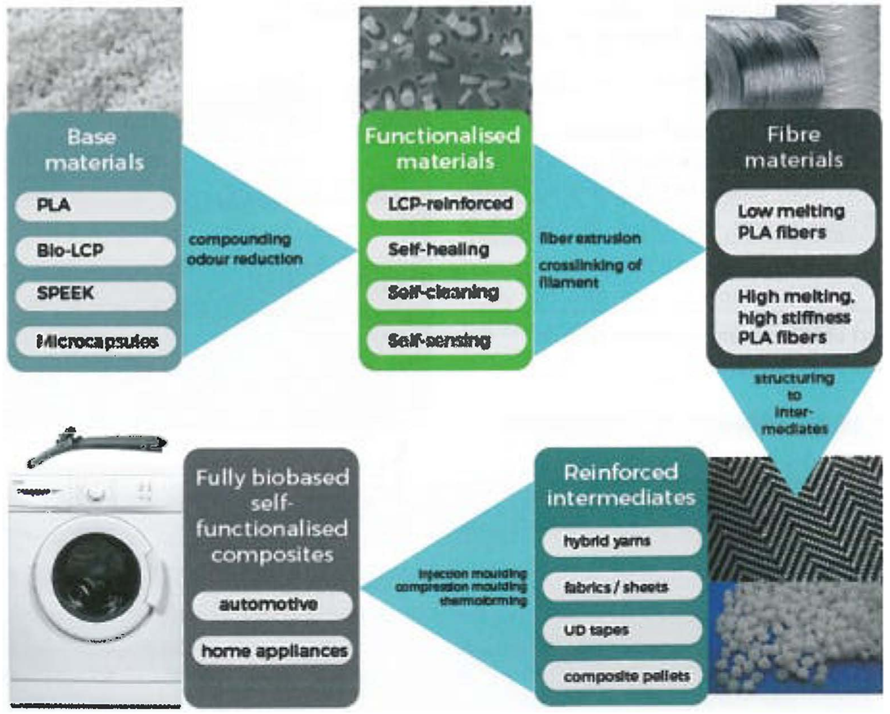


Fig. 2
Production of self-reinforced composite (1: low Tm PLA, 2: high Tm PLA)

Fig. 3
Value chain covered within the Bio4Self project



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.

Bio4Self proposed solution and approach

The described need is exactly the challenge being tackled within the H2020 project Bio4Self which aims at fully bio-based SRPCs.

Concept for producing PLA SRPCs

To produce such bio-based SRPCs 2 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 fibers. The low and high Tm PLA arte combining by producing hybrid yarns consisting of low Tm matrix fibers and high Tm reinforcement fibers. 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 bio-based composite material (Fig. 2).

In order to realize such bio-based SRPCs with a high quality, there is a need to develop bio-based polymeric materials with a high stiffness and high durability without impairing recyclability.

Value chain for SRPC production

To successfully realize 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 ranging from the production of functionalized materials, over the melt spinning, finally resulting in composite end products (Fig. 3).

Experimental setup and materials

At lab scale a multifilament extruder Spinmaster from Busschaert Engineering, Outrijve/Belgium, was used at a throughput of 4 kg/h. 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, a multifilament extruder was used in Svit (Vúchv a.s) at a throughput of 18.1 kg/h. The temperature was set at 245 °C. A yarn consisting of 100 filaments and a total titer of 340 dtex was produced.

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

L/D ratio spinneret	Modulus (GPa)
2	7.7
2.6	7.3
4	8.7

Cold draw ratio	Modulus (GPa)
1.8 ×	7.2
3.2 ×	7.8
6.1 ×	8.7

The high Tm PLA material (with a MFI (Melt Flow Index) of 10 g/10 min at 190 °C) was purchased from Total-Corbion-PLA. The low Tm PLA material (with a MFI of 15 g/10 min at 210 °C) was purchased from NatureWorks LLC, Minnetonka, MN/USA.

Results

Hydrolytical stability of PLA material

The limited hydrolysis stability of PLA was one of the most important key challenges to be tackled within Bio4Self. It is known that PLA is sensitive to hydrolysis which thus limits its use for durable applications. Therefore, various hydrolysis stabilizers were evaluated at concentrations going from 1-3 %. It was found that a 1 % addition already results in compounds with significantly enhanced hydrolysis stability. This was evaluated using an accelerated ageing test at 70 °C and 80 % relative humidity. Fig. 4 clearly illustrates that the molecular weight of the hydrolysis stabilized compound remains constant up to 240 hours of ageing, while the neat PLA compound has a complete drop in molecular weight already after 72 hours.

Optimization of the stiffness

The mechanical performance of the PLA SRPC will mainly depend on the performance of the high Tm reinforcement fibers. Therefore, the challenge for the high Tm filament extrusion is to produce filaments with a maximum stiffness, which will hence result in composites with a maximum stiffness as well. 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 1 and 2-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). In general, the multifilaments, with a titer of 5 dpf (dtex per filament), reached a stiffness of approx. 9 GPa.

Fig. 4
Enhanced hydrolysis stability of stabilized PLA compound

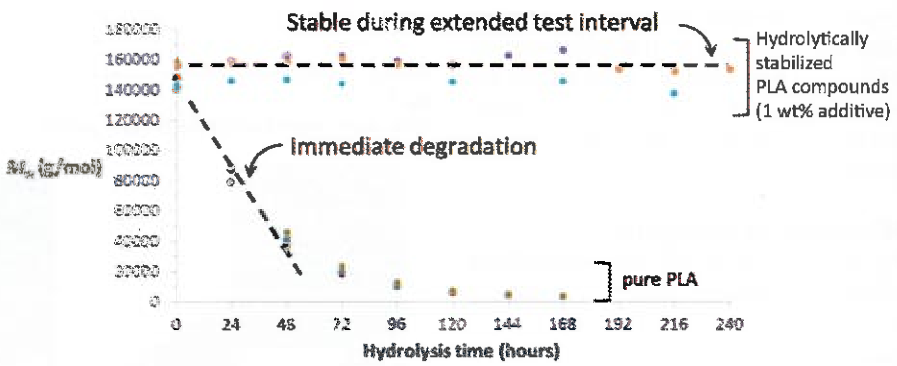
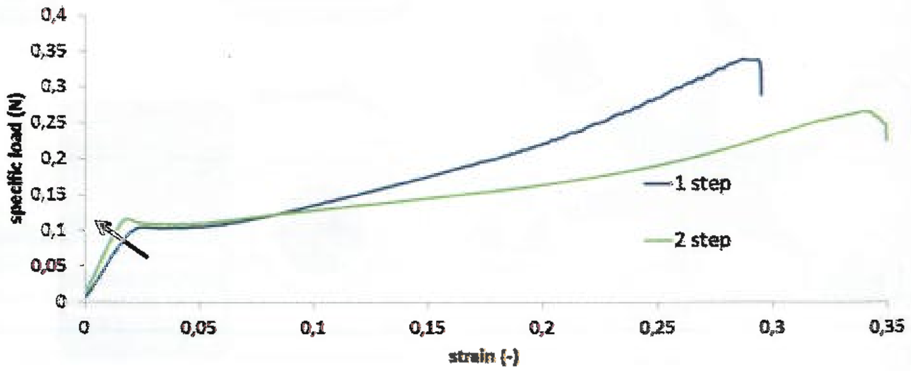


Fig. 5
1-step versus 2-step multifilament extrusion, arrow indicates increase in modulus



Next to the 1-step process, also a 2-step was investigated in which the extrusion was performed in a first step (at high take-up speed, 3,000 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 up-scaled at industrial scale by Fibrochem. This confirmed the advantages of a 2-step versus a 1-step process, resulting in a higher Young's Modulus (Fig. 5).

Processing of yarns to composites

Besides the high Tm PLA multifilaments, also low Tm PLA multifilaments were produced. Next, both fiber types were combined into a hybrid yarn. Optimization of the production speed, overfeeding rate, air pressure and air-jet nozzle resulted in a hybrid yarn with a homogeneous distribution between the low and high Tm PLA fibers.

Next, these hybrid yarns were processed into a woven fabric which was consolidated to a 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. 4 GPa).

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.

Outlook

Steps will be taken to further optimize 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 heat-setting step. Further, guidelines for the scaled up production of the high Tm filaments will be set. ■

Acknowledgements
The Bio4Self project has received funding from the European Union's Horizon 2020 research and innovation program under Grant Agreement No 685614.

Fraunhofer IAP

Cost-effective carbon fibers for light-weight construction

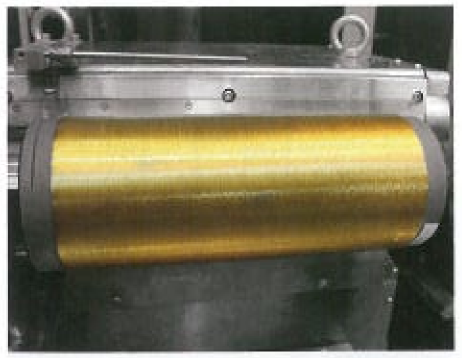
The ComCarbon technology from the Fraunhofer Institute for Applied Polymer Research IAP, Potsdam/Germany, will make it possible in the future to produce carbon fibers at low cost for the mass market. The institute presented this new technology at the leading aerospace trade fair, the ILA Berlin 2018, from April 25-29, 2018 in Berlin/Germany. Examples of applications for polymer-based lightweight construction and function-integrated plastics will also be presented.

Whether in airplanes, racing cars, high-performance yachts or bicycles – carbon fibers are the most advanced reinforcement fibers used to produce extremely lightweight composites. Nevertheless, penetrating mass markets, like the automotive, construction and other industries, which currently use glass and natural fibers, remains difficult. One of the main reasons are the high production costs of today's carbon fibers. A significant price reduction could contribute to a substantial increase in the use of carbon fibers in these sectors.

A meltable precursor

About half the cost of producing conventional carbon fibers is incurred in producing the precursor, the polyacrylonitrile fiber (PAN). This so-called precursor fiber cannot be melted and is therefore produced using an expensive solution spinning process. Now, Fraunhofer IAP has developed an alternative PAN-based precursor technology that saves around 60 % of the precursor costs. It is based on an inexpensive melt spin process using special, meltable PAN co-polymers that were developed especially for this purpose. Once they are converted to an unmeltable state, these cost-effective precursor fibers can then be processed into carbon fibers in the same way as conventional precursors using the established production routes.

PAN fibers are the perfect precursor material for the production of carbon fibers (© Fraunhofer IAP)



Using melt spinning saves on costs

There are several reasons why melt spinning has an enormous economic and ecological advantage over solution spinning. For one thing, it does not use any environmentally harmful solvents that have to be recycled at great expense. Eliminating solvents means that 100 % of the melted material can be spun, which enables significantly higher spinning speeds.

Conversion to carbon fibers

When producing carbon fibers, the precursor fibers must undergo stabilization and carbonization processes. To do this, the melt-spun precursor fibers are converted to an unmeltable state. Once this pre-stabilization is complete, the multifilament yarn is continuously fed into conventional stabilizing furnaces and carbonized at temperatures of up to 1,600 °C. ■

ComCarbon = registered trademark