Development of Bio-Based Self-Reinforced PLA Composites

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Keywords: Self-reinforced polymer composites, Commingling, Mechanical testing

Abstract. Self-reinforced polymer composites (SRPCs) are receiving increasing attention by the industry for lightweight applications. The polymers used for SRPCs today are derived from fossil resources. However, due to a limitation of resources, interest is growing regarding the use of new alternatives for petrol based polymers in form of bio-based ones. SRPCs combine high stiffness, high impact and high durability with impairing recyclability. In SRPCs the same polymer is used for the reinforcing and matrix phases. SRPCs can be manufactured by commingling reinforcing and matrix fibres with different melting temperatures. The use of commingled yarns allows the combination of a large variety of fibres and therefore a wide range of material properties.

Bio polymers

Fossil resources are limited [1]. Therefore research interest is growing regarding the use of new alternatives for petrol based polymers. More than half of bio-polymers produced are currently used in for packaging (39 %) and consumer goods (22 %). [1] There is no clear definition of a bio-polymer. In general bio-polymers are divided in four categories (see Fig. 1) [3]

Fig. 1: Classification of bio polymers according to [3]

A production capacity for biopolymers of 1.697.000 t has been recorded for 2014. The textile sector accounts for 186.000 t in 2014. Predictions indicate an increase to 560.000 t in 2019. The overall production capacity for bio polymers is expected to be increased to 7.847.000 t for 2019 [2]. Polylactic acid (PLA) is one of the most important bio polymers as it offers a wide range of configuration possibilities (e.g. molecular weight, crystallinity, L- and D-lactic-acid-ratio) [3]. Therefore it is used for this work.

Self-reinforced polymer composites

Fibre reinforced composites are two phase materials. The reinforcing phase is embedded in a polymeric matrix phase. Usually glass or carbon fibres are being used for the reinforcement. The mechanical forces are directed from the matrix into these fibres. This allows a major increase in mechanical properties of the matrix phase. As a result, fibre reinforced composites combine the advantage of high mechanical properties (strength and stiffness) with low weight. [4]

In self-reinforced polymer composites (SRPCs) the same polymer is used for the reinforcing and the matrix phase [5]. The concept was first introduced by Capiati and Porter in 1975 [6]. SRPCs combine high impact and high durability. However the density is lower compared to traditional filled polymers. Using the same polymer type also eases the recyclability of such composites [7].

The result of self-reinforcing polymers results in an increase of the following material properties:

- strength,
- stiffness,
- durability,
- and impact behaviour [8].

The most significant improvement is observed for the impact behaviour [8].

Another advantage of SRPCs is superior fibre-matrix-adhesion as fibre and matrix are made of the same material. The high chemical similarity leads to a strong composite as well as to a high nucleation density for the transcrystallization of the fibres into the matrix. The fibre-matrix-adhesion has a strong effect on the mechanical properties. Poor fibre matrix adhesion leads to peeling, cracking and reinforcement fibre pull-out. [8]

The use of thermoplastic reinforcing fibres for self-reinforced composites also introduces some disadvantages, as the reinforcing fibre loses its properties during heat exposure. In addition, the processing window for consolidation is limited. It has to be precisely controlled in order to receive the best mechanical properties. The small processing window (consolidation temperature and time) is the major challenge for producing SRPCs. The processing methods used commercially as well as in research are described in the following. [8]

The processes used to produce SRPCs are classified by the impregnation technique. Capiati and Porter produced their self-reinforced polyethylene (PE) using a Hot Compaction process in which the surface of the fibres is molten forming the matrix during consolidation [6]. It is possible to use fibres ore tapes (highly drawn film strips) for the reinforcing phase. The highly orientated fibres ore tapes can be processed into any form of textile (e.g. fabric or Non-crimp fabric). Pressure is applied during the consolidation to induce the flow of the molten surface to subsequently form the matrix. The temperature window for the Hot Compaction process is very low. The principle of the Hot Compaction process is illustrated in Fig. 2. This process is commercially used by Propex Fabrics GmbH & Co. KG, Gronau, Germany to produce the SRPC called Curv®. Curv® is a self-reinforced Polypropylene (PP). [4]

Fig. 2: Illustration of the Hot Compaction process for the production of SRPCs [4]

Another commercially used production process is based on coextruded material. Two polymers of the same type but different melting temperatures (polymer and its copolymer) are extruded simultaneously into fibres or tapes. This results in a core sheath structure. The difference of the melting temperatures widens the processing window. Only the sheath with the lower melting temperature is molten during the consolidation. The consolidation temperature is below the core melting temperature. The mechanical properties of the SRPCs commercially produced by coextrusion therefore outmatch the Hot Compaction process. The production process is illustrated in Fig. 3. [4]

Fig. 3: Illustration of the Coextrusion process for the production of SRPCs [4]

During both processes (Hot Compaction and Coextrusion) the reinforcing and matrix phase are produced simultaneously. Both are produced with equal temperatures as well as drawing ratios. However, the problem with bio polymers such as PLA is the temperature sensitivity. The Coextrusion of two different bio polymers is very difficult due to thermal degradation of the matrix phase. Therefore it is better to produce the reinforcing phase separately from the matrix phase. Two different processes are available to produce reinforcing and matrix phase separately from each other. This includes the Film-Stacking and the Commingling process [4].

The Film-Stacking process is illustrated in Fig. 4. The production principle is identical to the state of the art production process of the so called organic sheets. Organic sheets are a thermoplastic composites usually reinforced with a glass fibre fabric. Alternating layers of fabric and film (matrix) are stacked and consolidated using double belt presses [4]. To produce SRPCs with this production method the melting temperature of the film is lower compared to the reinforcing fibres. The use of matrix films allows the use of polymer grades different to the spinning grades. High pressures are required for a complete infusion of the reinforcing fabric, due to the high viscosity of the thermoplastic film [9].

Fig. 4: Illustration of the Film-Stacking process for the production of SRPCs [4]

SRPCs can also be manufactured using a Commingling process. The reinforcing fibres as well as the matrix fibres are mixed on a filament level during the Commingling process. The use of commingled yarns allows the combination of a large variety of fibres and therefore a wide range of material properties. In addition the melt flow paths of the matrix material are considerably lower compared to the Film-Stacking process [10]. COMFIL ApS, Gjern, Denmark currently produces SRPCs in form of high-tenacity PET mixed with low melting PET in form of yarn, fabrics, consolidated plates and rods/tapes. Self-reinforced Polypropylene (PP) is also available. [11] The production process of SRPCs using commingled yarns is illustrated in Fig. 5.

Fig. 5: Illustration of the Commingling process for the production of SRPCs

Experimental

The material provided for the development of self-reinforced PLA is procured directly in filament yarn form as part of the EU project BIO4SELF [12]. The PLA filament yarns have been melt spun by two different research facilities. The reinforcing fibres (High T_m) are provided by Centexbel, the Belgian research centre for textiles and plastics, Gent, Belgium. The matrix filaments (Low T_m) have been acquired from the AMIBM Aachen-Maastricht Institute for Biobased Materials, Maastricht, Netherlands.

The reinforcing fibres are mixed using a modular commingling machine at ITA. A mixing ratio of 50:50 is chosen. Prior to the commingling process both yarns are doubled to increase the comingled yarn count. Both filament yarns are delivered separately and commingled inside a mixing box using a comingling nozzle. By using compressed air to open and intermingle the fibres a hybrid yarn is produced. By increasing or decreasing the air pressure the turbulences increase or decrease. The amount of filament breaks as well as production costs rise with increasing air pressures. The quality of the yarn (fibre distribution and orientation) is also influenced by the overfeeding rate. Overfeeding is caused by the relative speed between the two pairs of delivery godets. No mixing of the filament yarns inside the nozzle is possible without overfeeding. In addition, the production speed constitutes a relevant process parameter for the hybrid yarn quality as well as production costs. The production process is shown in Fig. 6.

Fig. 6: The commingling process [9]

During the commingling trials speed, pressure and overfeeding rate are varied to identify a parameter set that offers best properties for the commingled yarn. Tab. 1 gives an overview on the used parameters. The air jet nozzle used is from by A.I.R. components GmbH, Gangelt, Germany. The parallel-plate mixing nozzle produces uniform interlaced structures in industrial filament yarns.

Tab. 1: Parameter set for commingling trials

	Variations
Pressure p [bar]	5, 6 and 7
Manufacturing speed v [m/min]	100, 150 and 200
Difference of overfeeding rate between fibres $\Delta OR_{rf/mf}$ [%]	0.5 and 2

Results

The yarns used in this paper are characterised regarding their thermal and mechanical properties. The melting temperature of the fibres have been analysed using Differential Scanning Calorimetry (DSC) from Mettler-Toledo GmbH, Greifensee, Switzerland. It was not possible to determine the melting temperature of the low melting PLA. Therefore, the melting temperature from the data sheet is given. The yarn count of the fibres is tested according to DIN EN ISO 2060. The tensile strength is analysed according to DIN EN ISO 2062 using a STATIMAT 4U from Textechno, Herbert Stein GmbH & Co. KG Textil Mess- und Prüftechnik, Mönchengladbach, Germany. The relevant fibre characteristics are presented in Tab. 2.

Tab. 2: Materials used for the experiments

	Low T_m PLA	High T_m PLA
SRPC phase	Matrix phase	Reinforcing phase
PLA grade	Ingeo™ Biopolymer 6302D	PURAPOL L130
PLA manufacturer	Nature Works	Corbion
Yarn count T_t [dtex]	211,87 ± 0,64	248,52 ± 3,17
Tensile strength σ_t [cN/tex]	10,22 ± 2,15	30,09 ± 2,84
Melting temperature T_m [°C]	125 - 135	176,99
Filaments produced by	AMIBM	Centexbel

The development of the hybrid yarns is successful. In total 54 different hybrid yarns are produced. The yarns are first examined visually. They are graded regarding the intermingling as well as the yarn structure (ondulation). The matrix fibres are coloured to ease the evaluation. Only poor intermingling results were achieved with air pressure of 5 bar. The yarns produced with 7 bar show high fibre ondulation and are therefore disregarded for composite production. No significant change of the intermingling and yarn structure is observed for the low manufacturing speed of 100 m/min. Therefore the yarns produced with low production speed are disregarded for composite production. The yarns used for composite production were produced with the parameters displayed in Tab. 3. The yarn count of the fibres is characterised according to DIN EN ISO 2060. The tensile strength is analysed according to DIN EN ISO 2062 using a STATIMAT 4U from Textechno, Herbert Stein GmbH & Co. KG Textile Mess- und Prüftechnik, Mönchengladbach, Germany.

Tab. 3: Manufacturing parameters and material properties of hybrid yarns for self-reinforced UD-composites

	A	B	C
Pressure p [bar]	6	6	6
Manufacturing speed v [m/min]	150	200	200
Difference of overfeeding rate between fibres ΔOR_{rf/mf} [%]	0,5	0,5	2
Yarn count T_t [dtex]	2070,71 ± 13,25	2070,10 ± 8,52	2079,81 ± 11,74
Tensile strength σ_t [cN/tex]	12,83 ± 0,97	12,33 ± 1,30	11,92 ± 1,38

It is shown that high production speeds during the commingling process can be used to produce hybrid yarns. The best mechanical properties of the three processing parameter sets displayed in Tab. 3 are received at low overfeeding rates (0.5 %) at a processing speed of 150 m/min. However, higher production speeds (200 m/min) do not lead to a significant loss in tensile strength. The impact of an overfeeding ratio of 2 %, between reinforcing and matrix fibre, also does not reduce the tensile strength of the hybrid yarn significantly.

Discussion

The research demonstrates the potential of PLA based SRPCs using the commingled yarn based process chain as during later processing a single material can be used. However a differentiation between the commingled yarns is difficult. Therefore, the production of UD composites from the hybrid yarns is required. The production of such composites is possible. The SRPCs are currently being tested according to DIN EN ISO 527-5. Previous results indicate high quality PLA SRPCs [13].

Conclusion and Outlook

It has been shown that hybrid yarns can be produced at high production speeds using the commingling process. The next research step includes the evaluation of different mixing ratios of reinforcing and matrix fibres. In addition the production of fabrics is investigated. The fabrics will also be consolidated and tested as well. The effect of the processing window of the consolidation process on the mechanical properties of the SRPC is going to be analysed. Further improvements on the material side may include adding nanofillers in order to increase mechanical properties. Additional research has to be conducted regarding the environmental impact of the biobased SRPCs.

Acknowledgments

The research leading to these results has received funding by the H2020 Funding Programme of the European Union under grant agreement n°685614. The BIO4SELF consortium consists of the 15 actual partners (with an EC budget) and further a group of 9 partners who expressed their support to the consortium via a Letter of Support. The latter group forms the so-called Innovation Support Group or ISG. The material used for this paper has been provided by Centexbel, the Belgian research centre for textiles and plastics, Gent, Belgium as well as the AMIBM Aachen-Maastricht Institute for Biobased Materials, Maastricht, Netherlands. We thank our partner COMFIL ApS, Gjern, Denmark who provided insight and expertise.

References

- [1] Bundesministerium für Ernährung und Landwirtschaft (BMEL): Nationale Politikstrategie Bioökonomie - Wachsende Ressourcen und biotechnologische Verfahren als Basis für Ernährung, Industrie und Energie, Berlin, 2014, p. 1-80.
- [2] IfBB - Institute for Bioplastics and Biocomposites: Biopolymers - facts and statistics, Hanover, 2015, p. 1-47.
- [3] H.-J. Enders, A. Siebert-Raths: Technische Biopolymere: Rahmenbedingungen, Marktsituation, Herstellung, Aufbau und Eigenschaften, München, Carl Hanser Verlag, 2009.
- [4] M. Neitzel, P. Mitschang, U. Breuer: Handbuch Verbundwerkstoffe - Werkstoffe, Verarbeitung, Anwendung, München, Carl Hanser Verlag, 2014.
- [5] Á. Kmetty, T. Bárány, J. Karger-Kocsis: Self-reinforced polymeric materials: A review, in: *Progress in Polymer Science*, 2010, p. 1288-1310.
- [6] N. Capiati, R. Porter: The concept of one polymer composites modelled with high density polyethylene, in: *Journal of Materials Science*, 10, 1975, p. 1671-1677.
- [7] J. Karger-Kocsis, S. Siengchin: Single-Polymer Composites - Concepts, Realization and Outlook: Review, in: *KMUTNB International Journal of Applied Science and Technology*, 7, 2014, p. 1-9.
- [8] W. Jia: Polylactic Acid Fibre Reinforced Biodegradable Composites, PhD Thesis, The University of Manchester, Manchester, 2015
- [9] T. Köhler, K. Vonberg, G. Seide, T. Gries: Self-reinforced composites made from PLA hybrid yarns, in: Simončič, Tomšič et al. (Hg.) 8-10 June 2016 – 16th World Textile Conference AUTEX, 2016, p. 1-7.
- [10] C. Cherif: Textile Werkstoffe für den Leichtbau, Techniken – Verfahren – Materialien – Eigenschaften, Berlin Heidelberg, Springer-Verlag, 2011.
- [11] COMFIL ApS, Gjern, Denmark: <http://www.comfil.biz/srp>, accessed 02.03.2017.
- [12] Project BIO4SELF: <http://www.bio4self.eu>, accessed 02.03.2017
- [13] S. Ramaswamy, M.-I. Popzyk, T. Gries: Development of biobased self-reinforced polymer composites - BioSRPC, in: Abschlussbericht zum Forschungsvorhaben IGF 90 EN am Institut für Textiltechnik der RWTH Aachen University, Aachen 2015, p. 1-112.