Materials Science Forum Vols. 825-826 (2015) pp 44-52
© (2015) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/MSF.825-826.44

Submitted: 2015-01-27
Revised: 2015-03-04
Accepted: 2015-03-13
Online: 2015-07-13

COST-EFFECTIVE MICROFIBRILLAR REINFORCED COMPOSITES FOR LIGHTWEIGHT APPLICATIONS

Krooß, Tim[1, a*]; Gurka, Martin[1, b]; Van der Schueren, Lien[2, c]; Ruys, Luc[2, d]; Fenske, Stefan[3, e];Lenz, Christopher[3, f];

[1] Institut für Verbundwerkstoffe GmbH, Germany
[2] Centexbel Textile Research Center, Belgium
[3] Institut für Textiltechnik Aachen, Germany

[a]tim.krooss@ivw.uni-kl.de, [b]martin.gurka@ivw.uni-kl.de, [c]Lien.VanderSchueren@centexbel.be, [d]luc.ruys@centexbel.be, [e]stefan.fenske@ita.rwth-aachen.de, [f]Christopher.Lenz@ita.rwth-aachen.de

Keywords: Thermoplastic composites, polymer fibers, melt spinning, blends, textiles

Abstract: Microfibrillar reinforced composites (MFC) are self-reinforced polymer-polymer composites, consisting of a cold drawn (fibrillized) phase in an isotropic matrix. They are manufactured via melt blending of two immiscible polymers with different melting temperatures, followed by a subsequent cold drawing and thermal annealing step. The present study examines the manufacturing of composite material out of melt-spun microfibrillar reinforced filaments. Polypropylene (PP) and Polyethylene terephthalate (PET) were chosen as the low-melting matrix and the high-melting reinforcement phase, respectively.

The filaments were woven to flat textile structures and processed to composites via hot pressing. They represent a bidirectional reinforced composite, comparable to other fiber reinforced polymers. To ensure optimized processing the influence of relevant parameters has been investigated with respect to mechanical properties of the MFC-filaments and the derived composites. In addition, the morphology was visualized by SEM imaging after all manufacturing steps. An important observation was that the reinforcing fibrils are still intact after thermal processing, leading to a significant increase in mechanical properties of the resulting composites. Quasistatic tensile tests show more than 100 % higher modulus and more than 50 % higher strength of the only 20 wt-% reinforced PET-PP composites compared to neat PP. The influence of the amount of PET reinforcement, the variation in processing conditions and composite layup were investigated. Additionally, an outlook on the melt-spinning of blends with Polyamide (PA) is given. In future work it is meant to show that a broad spectrum of tailored properties can easily be achieved by such polymer blends and composites outperforming existing homopolymers as well as thermoplastic composites like short glass-fiber-reinforced Polypropylene.

The material cost reduction thanks to adding cheaper mass-production polymers and the transfer onto conventional manufacturing lines is meant to ensure the feasibility of industrial production. The low density and excellent recycling options of these composites underline their potential for automotive and aircraft applications.

Introduction

Cold drawing of thermoplastic polymers introduces high molecular orientation and increased crystallinity, therefore significantly elevating properties like stiffness and strength of high performance melt-spun fibers [1]. However, the use of inorganic fibers in combination with thermosetting polymer matrices is currently favored due to their superior mechanical strength and better chemical resistance [2]. In contrast to thermoplastics most thermosetting polymers cannot be remolded due to cross linking which impedes the reuse and recycling of such composites [3,4], the

cross linking reaction is more time consuming and subsequent processing like forming or joining is more complicated [5]. Thus, thermoplastics like Polypropylene (PP) or Polyamide (PA) are widely used as matrices, e. g. for composites with glass fiber reinforcements. Nevertheless, economic manufacturing of glass fiber reinforced plastics remains a tough challenge, since processing requires semi-finished parts (e. g. preimpregnated fibers) and the recycling of composites including inorganic fibers still is complicated. In terms of mechanical recycling the composites usually are shredded, cut, milled or grinded and subsequently sorted in several fractions (from powders to different fiber lengths) to be reused as filler or reinforcements [6].

One possibility for sustainable material solutions are thermoplastic polymer-polymer composites, like microfibrillar reinforced composites (MFC). The concept of MFCs has been developed e.g. by Evstatiev and coworkers [7,8,9,10,11,12]. It is based on the melt blending of two thermodynamically immiscible thermoplastic polymers with a difference in melting temperatures and a subsequent drawing and annealing procedure, leading to a completely thermoplastic composite, being reinforced by fibrils of the higher melting polymer. In more detail, the three processing steps:

1) Melt blending of two thermodynamically immiscible polymers with a difference in their melting temperatures of at least 40 K followed by a
2) cold drawing of the extruded blend above the glass transition temperature of both polymers to achieve axial orientation of the phases (fibrillization) and
3) isotropization of the matrix polymer by a thermal annealing step between the melting temperatures of both components

leading to a material with micro-sized fibrils embedded in a continuous matrix [8,9]. After melt blending, a dispersion of the reinforcing polymer within the matrix of the lower melting polymer is created as illustrated in fig. 2a.

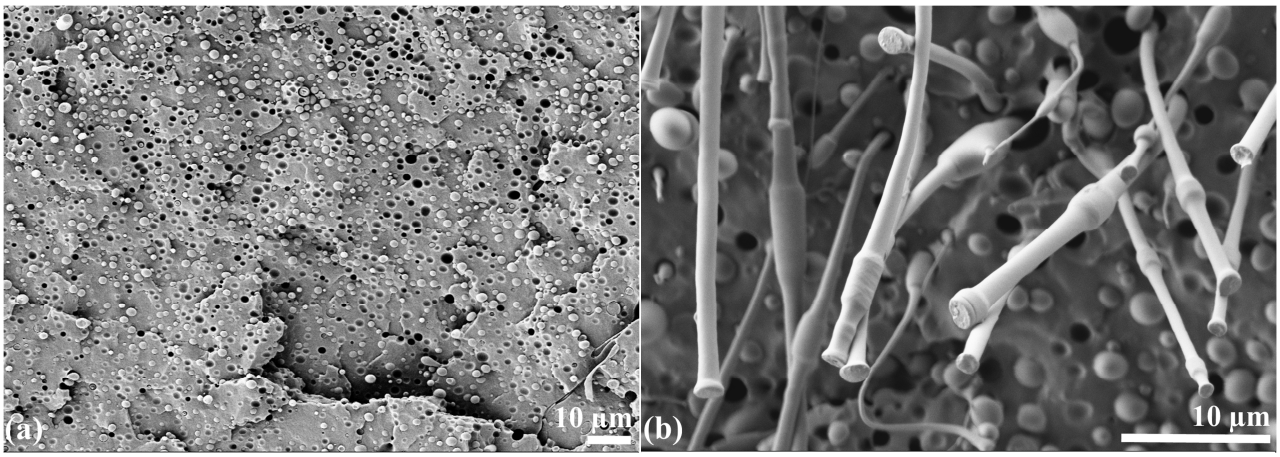


Figure 1: *Scanning Electron Microscopy Images of (a) melt blended immiscible polymers (PP/PET) and (b) formation of PET microfibrils.*

Within the cold drawing step the spherical particles are formed into ellipsoids and then into thin fibrils leading to an end-to-end coalescence [10] (fig. 2b). After thermal treatment above the matrix polymers´ melting point the latter is isotropizated while the reinforcing fibrils keep their drawn state. Compared with standard polymer composites, MFC demonstrate the following advantages:

- Reinforced by in-situ formed polymer nano- and micro-fibrils
- Ease of processing

- Reduced weight in comparison to other fiber reinforced composites
- Recyclability and repetition of the process [11]

Main issue of this technology is the transfer from a double screw extrusion line onto the semi-industrial single screw melt-spinning extrusion line and the optimization of isotropization steps related to best mechanical properties of the fibril reinforced unit.
This investigation deals with the manufacturing of highly orientated self-reinforced polymer-polymer composites on the basis of MFC out of Polypropylene (PP) and Polyethylene terephthalate (PET). Main objectives are:

1) the transfer of the MFC processing route from lab-scale to industrial scale melt-spinning systems
2) the optimization of post-processing regarding the final composite formation step, with regard to achievable mechanical properties stiffness and yield-strain
3) the demonstration of the potential of polymer-polymer composites

Experimental
Manufacturing of microfibrillar reinforced composite units consists of three main steps: (1) melt spinning extrusion and cold drawing, (2) weaving of drawn yarns into fabrics, (3) thermal processing (isotropization) of the woven fabrics via hot pressing. The compositions analyzed in this study were commercially available Polypropylene (Moplen HP400H) reinforced with 10 wt.- %, 20 wt.-% and 30 wt.-% of Polyethylene terephthalate (Polyclear® 1101). PP with a Melt Flow Index of 2.8 cm^3/10min and PET with an intrinsic viscosity of 0.83 dl/g was applied.
Preliminary work focused on the processing of precompounds produced on a double screw compounder and dry (= direct) blends on a semi-industrial melt-spinning monofilament extrusion line (Centexbel, Belgium). The monofilament extrusion was performed using a spin plate with 2 spin holes of 1.5 mm diameter at an extruder temperature of 270°C as to also melt the PET.
The monofilaments were processed using a Jakob Müller NH-2 narrow weaving machine to weave fabrics with a length of approximately 50 m. A weft hook was used to introduce the weft yarn and a plain weave was chosen for the weaving pattern. The resulting fabrics exhibited a width of 6.5 cm with a warp density of 18 threads per cm and a weft density of 9 threads per cm at a weaving speed of 200 weft insertions per minute.
To define processing conditions the determination of melting peaks via Differential Scanning Calorimetry (DSC) and structural observation via Scanning Electron Microscopy (SEM) of the yarns were performed. Hence, a soxhlet experiment was executed to remove the PP phase and expose the PET fibrils. The medium used to extract the Polypropylene phase was Xylol which was heated up to 115°C. Observation of the extracted fibrils for single fabrics and composites with 9 layers was done by SEM. Evaluation of the mechanical properties has been executed via quasistatic tensile testing and 3-point-bending. The composites were cut into rectangular samples and tested on a Zwick/Roell testing machine with a 5 kN load cell. Testing speed was 5 mm/min for the tensile tests and 1 mm/min for the bending test. The Young´s Modulus was calculated between 0.5 % and 0.75 % strain, Flexural Modulus was calculated between 0.3 % and 0.5 %. At least 5 samples were tested for each composition and test method.

Results And Discussion

The maximum draw ratio of the melt-spun filaments, indicating the drawability and thus the potential for elevated mechanical properties, was similar for both the precompound and dry blend and moreover comparable to the maximum draw ratio of neat PP. The resulting tenacity of the filaments at varying draw ratio is presented in the fig. 2 below. An important fact observed was that the drawn blends show a higher tenacity compared to neat PP yarns with similar draw ratio. Thus, the substitution of PP by PET did not lead to a decrease of mechanical properties but increased them. No difference in tenacity between the dry blend and the precompound was observed. This shows that double screw mixing is not needed for processing PP/PET blends and evidences the feasibility of processing the drawn blends on industrial standard textile spinning machinery.

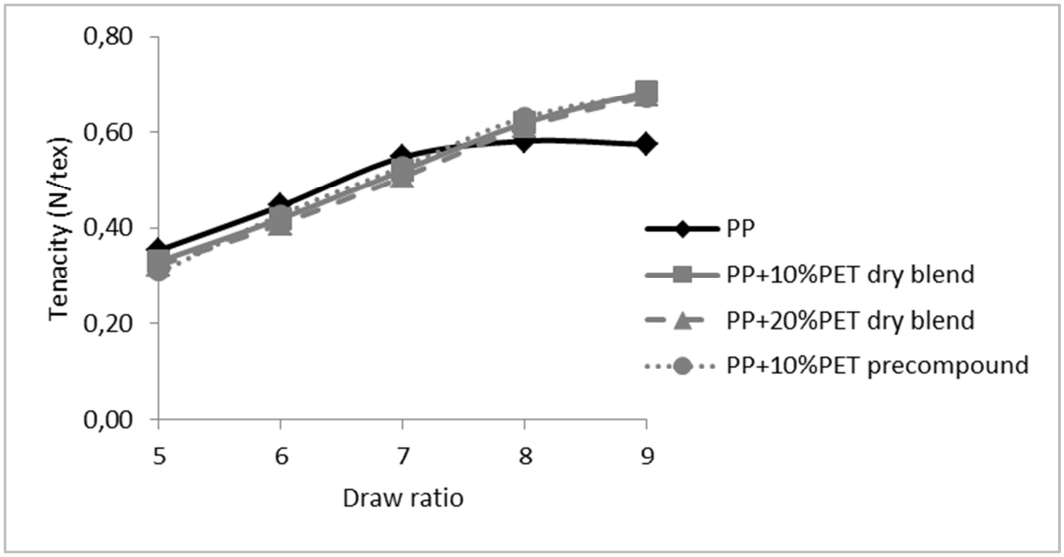


Figure 2: *Tenacity as a function of draw ratio for microfibrillar reinforced PP.*

For thermal processing into a composite with highly orientated PET fibrils, the end of the melting peak of the matrix phase and the beginning of the melting peak of the reinforcement phase is relevant. The observations from DSC show that due to the PET in the yarns the melting peak of the Polypropylene is slightly elevated up to 172°C. The end of the visible enthalpy area can be determined at approx. 183°C. These temperatures define the possible processing range (fig. 3).

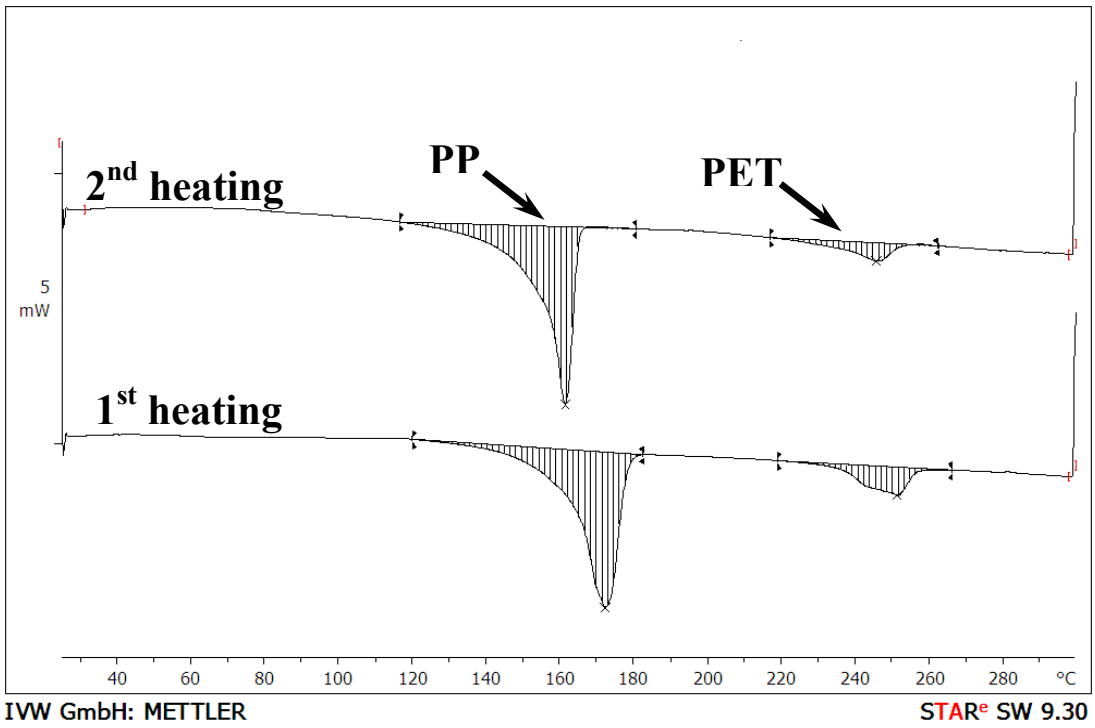


Figure 3: *DSC graphs of PP/PET 70/30 with draw ratio of 9.*

Conclusions from the DSC experiments can be drawn as follows: (1) drawing of PP/PET monofilament yarns introduces structural order for both the PP and the PET phase, indicated by shifts of the melting enthalpies up to higher temperatures, thus (2) more energy is necessary to receive appropriate melting and isotropization of the drawn Polypropylene phase compared to the undrawn polymer, (3) the thermal processing will therefore cause relaxation of the drawn monofilament yarns or shrinkage, respectively, due to melting of the PP phase and (4) the processing window for the fabric consolidation into a composite can be determined over a range of at least 40 K.

Considering the shrinkage of the fabrics, the consolidation process was executed without a closed mold to enable a fixation between the hot plates of the press. Thickness of the samples was regulated by distance plates with a thickness of 1.5 mm; the applied pressure of 3 MPa is meant to ensure sufficient clamping of the fabrics during heating; consolidation time first was set at 60 min.

Besides the 20 wt-% and 30 wt.-% PET reinforced fabrics, reference samples of neat PP monofilaments have been processed. After the hot pressing into composites the samples were prepared for SEM analysis by extracting the PP phase. The reinforcement structure is illustrated in figure 5. The images clearly show an intact reinforcement structure.

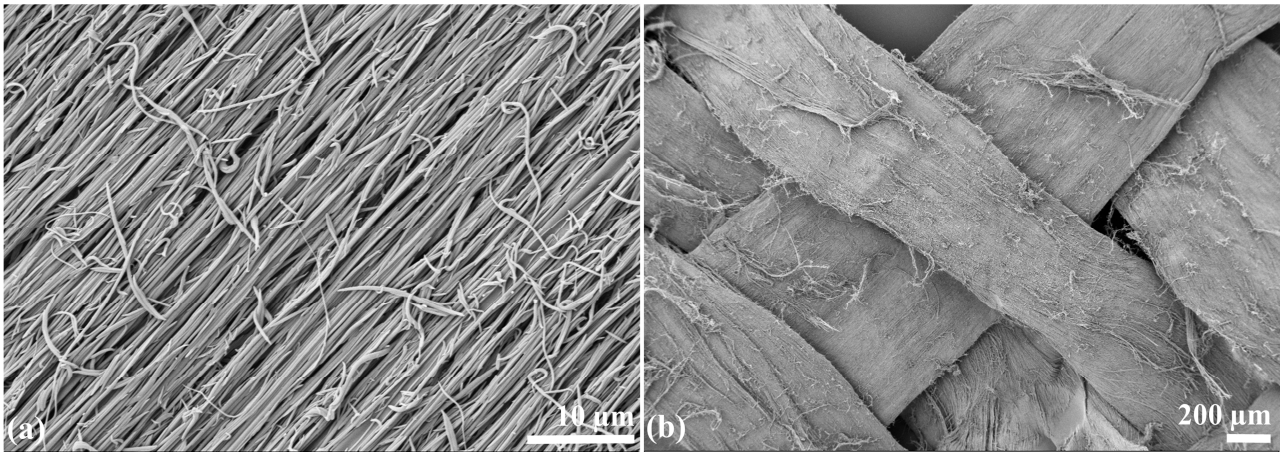
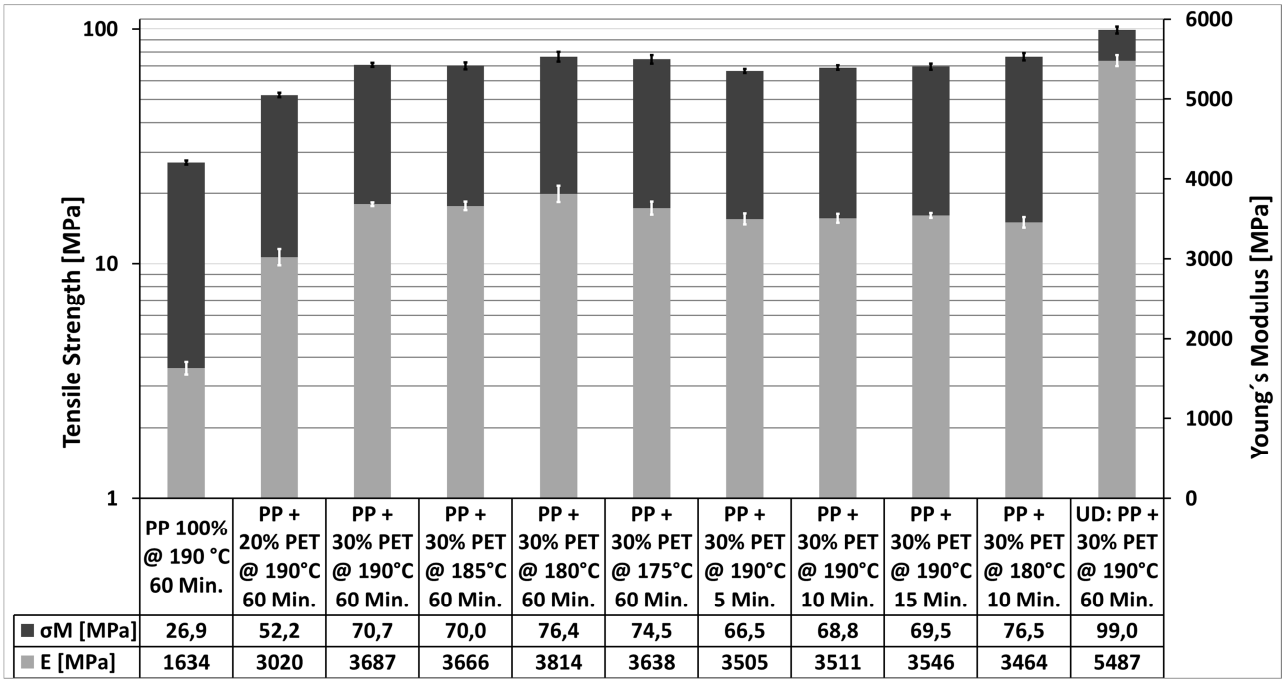


Figure 4: *SEM images of composites with a draw ratio of 5 after soxhlet extraction of the PP phase; (a) close-up of PET fibrils (magn. 5000x), (b) overview of PET structure (magn. 100x).*

The reinforcing fibrils kept the woven structure and were successfully transferred into the composites. The fibrils that were formed in the melt-spinning process feature a high aspect ratio showing an average thickness of approximately 240 nm and seem to be endless. Furthermore, no overall breakage of the PET fibrils was observed. At the pressure of 3 MPa the fabrics were not given a chance to contract dramatically until the melting state of the PP phase was reached. Although contraction occurs in all directions, it was possible to receive the desired geometry for testing samples. The achieved mechanical properties were then evaluated within static tensile tests (Fig. 5).

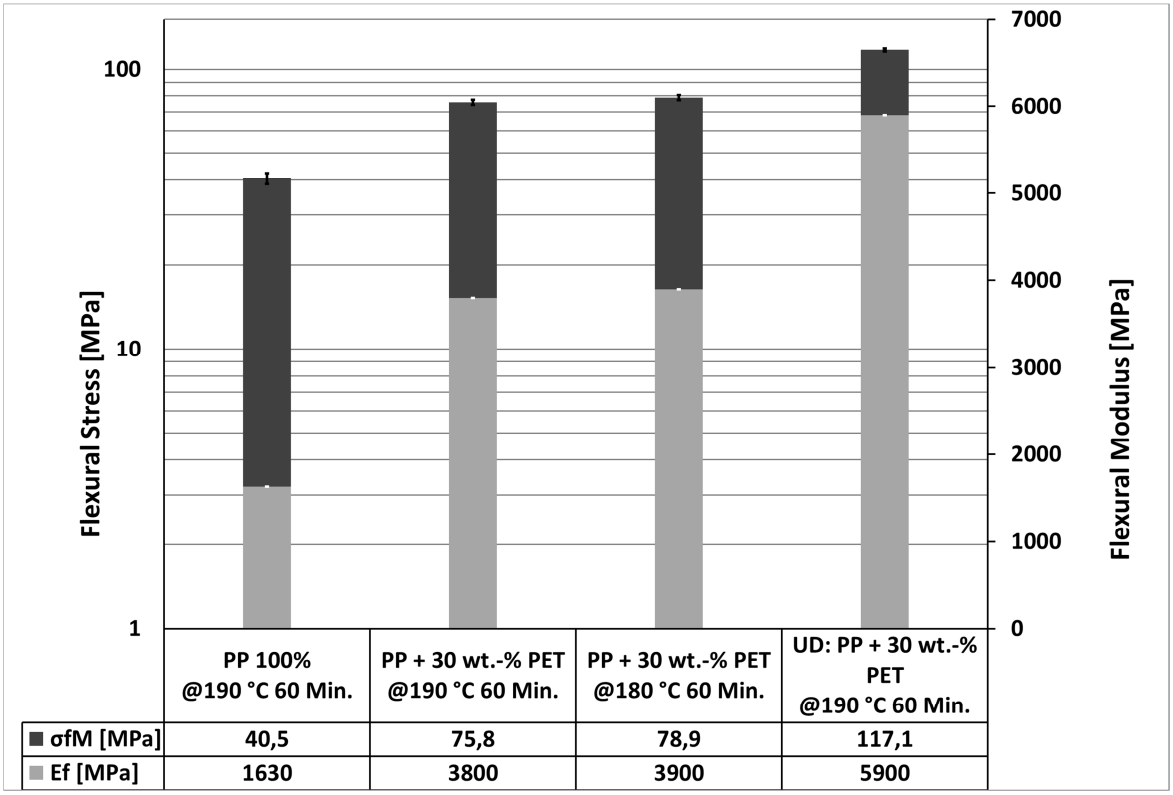
The results from tensile testing show the elevated properties for the reinforced composites compared to neat Polypropylene. It is underlined that both the 20 wt-% PET reinforcement and drawing of the filaments lead to an increase of modulus by more than 100 % and an increase in tensile strength by more than 50 % after thermal processing. An increase of the PET reinforcement by 10 wt.-% further elevated the properties of the final composites due to more reinforcing fibrils in the PP matrix. Under the same processing conditions the modulus of 30 wt.-% reinforced Polypropylene was increased by more than 600 MPa, while the tensile strength at break was increased up to 70 MPa.

To analyze the effect of variation of the processing temperature for the 70/30 composition, processing temperatures were set between 175°C and 190°C, related to DSC results, and stepwise increased by 5 K. Other processing parameters were kept constant. On a second variation level, focus was set on the optimization of processing times. The fabrics were inserted into the preheated press and then consolidated for 5, 10 and 15 minutes, respectively, at the reference temperature of 190°C. The summary of tensile and flexural properties is shown in Fig. 5.



	PP 100% @ 190 °C 60 Min.	PP + 20% PET @ 190°C 60 Min.	PP + 30% PET @ 190°C 60 Min.	PP + 30% PET @ 185°C 60 Min.	PP + 30% PET @ 180°C 60 Min.	PP + 30% PET @ 175°C 60 Min.	PP + 30% PET @ 190°C 5 Min.	PP + 30% PET @ 190°C 10 Min.	PP + 30% PET @ 190°C 15 Min.	PP + 30% PET @ 180°C 10 Min.	UD: PP + 30% PET @ 190°C 60 Min.
σM [MPa]	26,9	52,2	70,7	70,0	76,4	74,5	66,5	68,8	69,5	76,5	99,0
E [MPa]	1634	3020	3687	3666	3814	3638	3505	3511	3546	3464	5487

Figure 5: *Tensile properties of differently processed MFC.*



	PP 100% @190 °C 60 Min.	PP + 30 wt.-% PET @190 °C 60 Min.	PP + 30 wt.-% PET @180 °C 60 Min.	UD: PP + 30 wt.-% PET @190 °C 60 Min.
σfM [MPa]	40,5	75,8	78,9	117,1
Ef [MPa]	1630	3800	3900	5900

Figure 6: *Flexural properties of differently processed MFC.*

As supposed, the tensile strength and modulus were slightly improved when processed at 180 °C. At a temperature of 175°C the mechanical properties begin to decrease. Although there is a slight decrease of the tensile properties of short processed composites, the combination of downshifted temperature and short consolidation time leads to acceptable values: At 180°C and consolidation time of 10 minutes a modulus of 3.4 GPa and a tensile strength at break of 76.5 MPa was measured for the 30 wt.-% reinforced Polypropylene. The manufactured UD-composites, obtained via filament winding, exhibit a Young´s modulus of approximately 5.5 GPa and a tensile strength of 100 MPa.

The flexural properties of selected composites are shown in fig. 6. With a flexural modulus of more than 3.9 GPa the composites processed at 180°C even outmatch self-reinforced Polypropylene materials like Curv® [12]. Again, the values for unidirectional winded composites indicate the further potential of this technology. In this case the flexural modulus was elevated by more than 260 % compared to the neat polypropylene composite and by more than 50 % compared to bidirectional reinforced composites. The summary of the results thus can be defined as follows:
The amount of fibrils (PET content) and the draw ratio of melt-spun yarns significantly influence the mechanical properties of MFC structures after thermal processing. The modulus of the composites is mainly influenced by the processing temperature and consolidation time; at lower temperatures the tensile strength is not significantly influenced; reducing the processing temperature lead to an increase of both, tensile and flexural properties. The orientation of filaments can be adjusted to several requirements by different weaving patterns. For this specific example, a cheap composite material can be obtained by using commodity polymers which are combined into a composite with good performance (PP: approx. 1.400 €/ton; PET: approx. 1.200€/ton; recycled PET: approx. 840-1.000 €/ton [13]). Additionally to these results, the PET amount is being further increased to 50 wt.-%. First lab-scale tests resulted in maximum tensile strength of more than 140 MPa for unidirectional composites.

Conclusions

The current investigation aimed at the development of a process line for fiber-reinforced polymer-polymer composites out of woven yarns. As illustrated, the spinning process was adjusted relating to the effective production of microfibrillar reinforced filaments out of PP with 20 wt.-% and 30 wt.-% of PET. One objective was the transfer of this MFC technology from a double screw extrusion line onto the semi-industrial single screw melt-spinning extrusion line. This goal was successfully achieved. Further processing via cold drawing did lead to elevated properties of the extruded monofilaments, which were subsequently woven to bidirectional fabrics. The results from tensile testing show that a 20 wt.-% PET reinforcement can significantly elevate the properties of Polypropylene. Further adjustments of fibril content up to 30 wt.-% PET and processing parameters additionally elevated the composites properties. The manufactured composites offer mechanical properties that are comparable to short glass fiber reinforced PP materials and self-reinforced PP like Curv®, while partially being substituted with a low cost mass production polymer (PET).
It was shown that blending and processing of cheap and recyclable polymers on this process line can mean a significant advantage for industrial production of thermoplastic units. Further investigations will concentrate on the processing of mono- and multifilament yarns and fabrics through which elasticity and strength of the later composites can be adjusted. Moreover, experiments on different material compositions with highest possible fiber content and out of different polymer types will be investigated. Also the use of PP/PA blends within this process line was possible with PA amounts up to 40 wt.-%. The development of PP/PA films will be investigated in future studies.
The increase of mechanical properties in the sense of microfibrillar reinforcement on the one hand and the potential morphology formation on the other hand are aiming at the development of blends with ‘in-situ tailored’ properties for composite applications. By a profound processing knowledge, thermoplastic polymer blends and composites can easily be generated and tailored to specific unit requirements.

Acknowledgement
The project was financed by the Bundesministerium für Wissenschaft und Technologie as an IGF intention with the number 78 EN/2 within the Program for Advancement of the Industrial Community of Research and Development (IGF)/CORNET(Collective Research Networking).

References

[1] W. H. Carothers, J. W. Hill, Studies Of Polymerization And Ring Formation: XV. Artificial Fibers From Synthetic Linear Condensation Superpolymers, Journal of the American Chemical Society (1932), pp. 1579–1587.

[2] B. Arnold, Werkstofftechnik für Wirtschaftsingenieure, first ed., Springer Vieweg, Heidelberg, Dordrecht, London, New York, 2013.

[3] H. F. Brinson, L. C. Brinson, Polymer Engineering Science and Viscoelasticity – An Introduction, Springer Science+Business Media, New York, 2008.

[4] S. J. Pickering, Recycling technologies for thermoset composite materials—current status. – School of Mechanical, Composites Part A: Applied Science and Manufacturing 37 8 (2006), pp. 1206-1215.

[5] A. Gillot, From carbon fibre to carbon-fibre-reinforced thermoplastics, JEC Composites Magazine 71 (2012), pp 60-62.

[6] A. Hedlund-Aström, Model for end of life treatment of polymer composite materials, Doctor Thesis (2005).

[7] M. Evstatiev, S. Fakirov, Microfibrillar Reinforcement of Polymer Blends, Polymer 33 4 (1992), pp. 877–880.

[8] S. Fakirov, D. Bhattacharyya, R. J. Shields, Nanofibril reinforced composites from polymer blends, Colloids and Surfaces A: Physicochem. Eng. Aspects 313–314 (2008), pp. 2–8.

[9] K. Friedrich, M. Evstatiev, S. Fakirov, O. Evstatiev, M. Ishii, M. Harrass, Microfibrillar reinforced composites from PET/PP blends: processing, morphology and mechanical properties, Composites Science and Technology 65 (2005) 107–116.

[10] D. Bhattacharyya, S. Fakirov, Synthetic Polymer-Polymer Composites, first ed., Hanser, Munich, 2012, pp. 353–400.

[11] S. Fakirov, M. Evstatiev, K. Friedrich, From Polymer Blends to Microfibrillar Reinforced Composites, in: Paul Bucknall, C.B Bucknall (Eds.), Polymer Blends, John Wiley & Sons, New York, 2000, pp. 455–475.

[12] Information on http:// www.curvonline.com

[13] Information on http:// www.kiweb.de

20th Symposium on Composites
10.4028/www.scientific.net/MSF.825-826

Cost-Effective Microfibrillar Reinforced Composites for Lightweight Applications
10.4028/www.scientific.net/MSF.825-826.44