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# Rheological and Mechanical Behavior of Long-Polymer-Fiber Reinforced Thermoplastic Pellets

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**ABSTRACT:** Polymer–polymer materials consist of a thermoplastic matrix and a thermoplastic reinforcement. Recent research activities concentrate on the manufacturing of semi-finished polymer–polymer materials in other shapes than the commercially available tapes and sheets. In particular, a pellet-like form provides the possibility of processing the polymer–polymer material by injection and compression molding. Nevertheless, the thermoplastic reinforcement is vulnerable to excessive heat and the processing usually needs special attention. The current study investigates the processing of long-polymer-fiber reinforced thermoplastic pellets, namely polypropylene-polyethylene terephthalate and a single-polymer polyethylene terephthalate, by extrusion for subsequent compression molding applications. The flow characteristics of the material as well as the preservation of the polymer reinforcement can be handled by accurate temperature control. The tensile and impact properties decrease with increasing process temperature though. Moreover, the results prove that the use of a common long-fiber reinforced thermoplastic process chain is applicable to the newly developed polymer–polymer material. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39716.

**KEYWORDS:** composites; molding; extrusion; rheology; mechanical properties

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## INTRODUCTION

First attempts to manufacture polymer–polymer, and especially single-polymer, composites were made in the 1970s.[1,2] In contrast to standard fiber reinforced polymer composites that mainly benefit from the combination of a polymer matrix and inorganic fibers, polymer–polymer materials consist of a polymer matrix phase and a polymeric reinforcement. The used components can be chosen amongst the variety of all polymers available on the market, whereas mainly thermoplastic versions are nowadays in use[3–5] and are subject matter of current research activities.[6–12] For conforming to the term self-reinforced polymer (SRP), matrix and reinforcement of such materials have to originate from the same polymer type (e.g. polypropylene, PP, matrix, and PP fiber). In literature and recent research, the definition of SRPs refers also to reinforced materials that consist of a polymer matrix and reinforcement from the same polymer family (e.g. for polyolefins: a combination of high density polyethylene, HDPE, and PP).[13] To distinguish between these types, the concurrent definition of single-component (same polymer) and multicomponent (same polymer family) SRP is applied. Further classifications respect the production process steps (single or multi) and the spatial distribution of the reinforcement (1D, 2D, 3D).[9]

The polymer fiber shrinkage is one of the major challenges during subsequent processing of polymer–polymer composites.[14] Polymer shrinkage occurs through the relaxation of an oriented polymer structure because of internal forces. For polymer-reinforced materials, mainly the triggering of shrinkage by thermal processes is of relevance. In the first place, shrinkage within a material is predetermined by the respective manufacturing process. For the manufacturing of polymer fibers, as used in SRP composites, thermoplastic polymers are molten, spun, and drawn to gain certain properties. An additional drawing process of a fiber in cold state causes a higher orientation of the molecular chain and a higher perfection of crystallites. The cold-drawing process consequently results in increased tensile properties, but also the danger of shrinkage of the fiber is higher because of higher frozen-in relaxation forces. Besides the processing, the fiber material, including the crystallite orientation and the molecular structure of amorphous regions, and the material's thermal history influence the shrinkage behavior.[15,16] Thermally triggered shrinkage usually occurs below the melting temperature of semi-crystalline thermoplastics. For fibrous PP materials, a high shrinkage was reported between 140°C and 155°C, which is close to the respective melting temperature.

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**Table I.** Investigated Materials in the Current Study

| Material | Reinforcement fraction (wt %) | Reinforcing fiber material | Pellet length (mm) | Manufacturer |
|---|---|---|---|---|
| PP-PET30 | 30 | PET | 7 | Celstran GmbH, Germany |
| srPET | 31 | PET | 5 | Comfil ApS, Denmark |

The shrinkage related softening effect for PP was even observed at an earlier state beginning from 80°C to 90°C.[17] PET fibers revealed a softening around their glass transition temperature at 65°C, whereas the shrinkage was monitored to be linearly increasing from this point with increasing temperature.[10,13]

Commercial SRP materials are already available from a small amount of manufacturers but they are all based on polyolefins and are only available as sheets or tape-like form.[18] In contrast to the shapes of available products, recently developed polymer fiber reinforced thermoplastic pellets offer the possibility for injection and compression molding process with a higher freedom of design. Nevertheless, the application of standard machinery using screws for heating may significantly harm the reinforcement and decrease its integrity because of the high shear forces of the commonly applied screws. Therefore, the objective of this study was to investigate the feasibility of novel self-reinforced pellets in a long-fiber reinforced thermoplastic (LFT) compression molding process with standard extrusion equipment. Furthermore, the research results help to evaluate if recently developed special intrinsic heating methods are categorically needed in extrusion processes for those novel and highly sensitive materials. The mentioned heating methods make use of additional particulate susceptors in the matrix which can be contactless heated by means of electromagnetic radiation.[19–21] Nevertheless, the aforementioned heating techniques generate higher investment and material costs, which can probably prevent an application of the investigated materials in a future product.

This study revealed a general feasibility of the polymer–polymer materials to be processed on standard extruding machinery. The meltable reinforcement is affected by the shear forces, but the damage can be limited and the high mechanical performance could be maintained. However, the successful application is strongly related to the processing temperature, the viscosity of the composite, and the complexity of the desired part.

## EXPERIMENTAL

A self-reinforced all-polyester system (srPET), consisting of an amorphous polyethylene terephthalate (PET) matrix and crystalline PET fibers, as well as a polypropylene-polyethylene terephthalate (PP-PET30) compound were applied in this feasibility study (Table I). The PP-PET30 compound (Celstran GmbH, Germany) was manufactured in a melt impregnation process and served as model system providing a large temperature gap

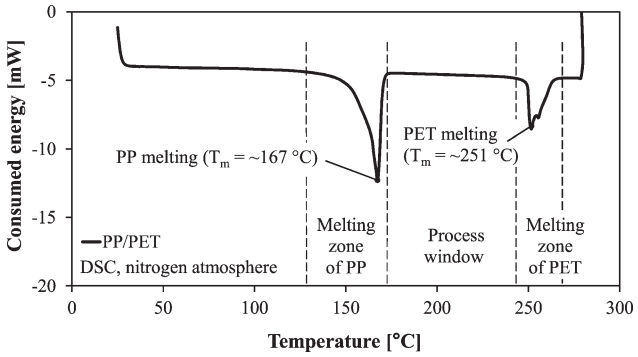


**Figure 1.** Difference in melting temperature of PP matrix and PET fiber recorded by differential scanning calorimetry.

between PP matrix and PET fiber melting point (Figure 1). Thus, a processing without fiber damage was expected. The srPET (Comfil ApS, Denmark) was manufactured by commingling with subsequent consolidation and pelletizing. Each compound contained a fiber fraction of approximately 30 wt %. Both materials were dried at 40°C for a minimum of 24 h prior to the processing in the extruder.

A Kannegiesser KMH60S (Kannegiesser, Germany) single-screw extruder was applied for the pellet melting prior to compression molding. By adjusting the extruder's six heating zones, distinct extrudate temperatures could be realized. All other parameters, like the back pressure or the screw speed, were kept on a constant level (Table II). The amount of extrudate, which was heated within a cycle of approx. 210 s, was 500 g per shot. The extrudate was transported and placed manually into the mold.

For the molding of the preheated extrudate, a Dieffenbacher hydraulic press (J. Dieffenbacher GmbH, Germany) was able to realize a maximum press force of 8000 kN (800 t). Several molds were used for the trials, which included a shear edge mold for a sheet (540 x 540 $mm^2$) and a complex shaped tool with ribs for the manufacturing of an automotive demonstrator part. An exemplary process cycle is given in Figure 2.

The experimental series contained an analysis of the compounds' rheological properties, in particular the viscosity and the shear rate in reference to the process temperature. The viscosity was measured by a rheometer setup that was mounted in the press (Figure 3). The setup consisted of two disks with a diameter of 250 mm. The hot composite extrudate was placed between the heated disks (160°C) and compacted. The disk temperature was chosen higher than the standard mold

**Table II.** Applied Extruder Parameters

| Property | Value |
|---|---|
| Max. pressure | 150 bar |
| Nozzle diameter | 55 mm |
| Speed | 10 $min^{-1}$ |
| Back pressure | 40 bar |
| Material weight | Approx. 500 g |
| Cycle time | 210 s |

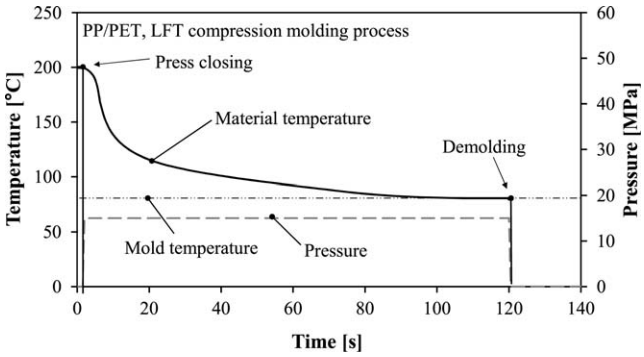


**Figure 2.** Process parameters used for the manufacturing of compression molded PP-PET compounds.

temperature for these polymer matrix systems to enable an isothermal material flow without freezing effects on the disk edges. By analyzing the obtained press data, which included closing speed $v$, press force $F$, and distance $h$ between the disks, the shear rate as well as the viscosity could be calculated according to the given equations [eqs. (1) and (2)].[22,23] The closing speed $v$ was preset to 5 mm/s and a maximum force $F$ of 1500 kN was applied after complete closure.

$$\text{Shear rate } \dot{\gamma} = \frac{2vR}{h^2} \tag{1}$$

$$\text{Viscosity } \eta = \frac{2Fh^3}{3\,\pi\,vR^4} \tag{2}$$

For the mechanical analysis, tensile tests with cut samples from compressed sheets according to DIN EN ISO 527 and dart impact experiments according to DIN EN ISO 6603-2 were performed. Furthermore, specimen bars were cut for the use with a Charpy impact test rig according to DIN EN ISO 179-1eA.

A Zwick Roell 1474 universal testing machine (Zwick Roell, Germany) was applied for the standard mechanical tensile tests. A minimum of eight specimens per material and process temperature level were examined at a test speed of 5 mm/min. The elastic modulus was obtained within a range up to 1% strain by a macro extensometer. A 10-kN load cell was applied for the measurement of the maximum force.

As polymer–polymer composites are known for their high impact properties, Charpy impact tests were performed. They served to reveal whether the used higher extrudate temperature

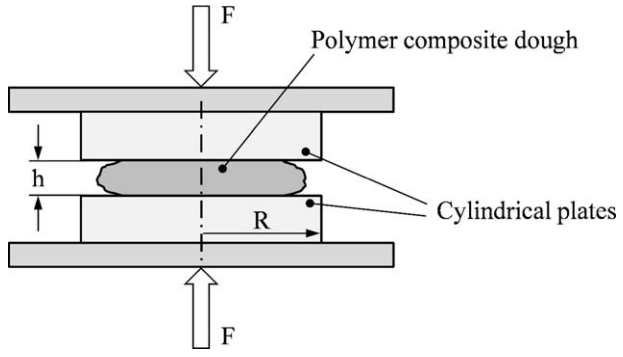


**Figure 3.** Built-in-press rheometry setup.

**Table III.** Investigated Extrudate Temperatures

| Material | Investigated extrudate temperatures (°C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| PP-PET30 | 170[a] | 180 | 190 | 200 | 220 | - | 250 | - |
| srPET | - | 180[a] | - | 200[a] | 220 | 240 | - | 260 |

[a] Revealed to be not feasible for extruder processing.

negatively influenced the impact behavior of the matrix and should prove the vanishing of the fibers with higher process temperature. The bars obtained from the sheets were notched according to DIN EN ISO 179-1eA. The Charpy pendulum was equipped with a 15 J hammer and each experimental series consisted of 10 samples. The notch impact strength acN was calculated from the measured impact energy ($W_I$), the loss energy ($W_L$), and the sample cross section ($a \times b$) according to the following equation:

$$a_{cN} = (W_I - W_L) \cdot (a \cdot b)^{-1} \cdot 10^3 \ \text{kJ/m}^2 \tag{3}$$

Besides the Charpy impact experiments, the impact performance of SRP was analyzed with a dart impact test rig. The composites were tested in sheet-like shape with the dimensions of 80 × 80 mm$^2$ and a thickness of 2.3 mm. A cylindrical impactor with a diameter of 20 mm was applied on the vertical sledge with a total weight of 10.357 kg. At a height of 0.987 m, this weight results in an impact velocity of 4.4 m/s and equals to a maximum impact energy of 100.26 J, which conforms to the parameters given by the standard DIN EN ISO 6603-2. The maximum force and the energy at maximum force $W_{max}$ were evaluated by the help of a 60 kN load cell.

## RESULTS AND DISCUSSION

### General Observations and Rheometry Results

For both investigated compounds, various extrudate temperatures have been tested for their feasibility. The range for PP-PET30 included temperatures from 170°C to 250°C, the srPET experiments covered the range from 180°C to 260°C (Table III). The viscosity was revealed to be too high in case of an extrudate temperature of 170°C for PP-PET30. The extruder was not able to transport the high viscous material sufficiently. An identical behavior was observed with srPET at 180°C and 200°C.

In the case of PP-PET30, all examined extrudate temperatures led to a dough-like viscous material, whereas the srPET system was found in a honey-like, low viscous state at 260°C. Lower temperatures resulted in high viscous behavior for the polyester system as well. The very low viscosity of srPET at higher temperatures was attributed to an excessive reinforcement melting. The qualitative impression of the viscosity changes caused by the different process temperatures was verified by a quantitative rheological analysis. Within this analysis, the PP-PET30 system revealed a maximum viscosity below 1000 Pas, which is in the range of competing glass-fiber filled PP compounds (Figure 4).[24] The viscosity declined with increasing extrudate temperature, whereas nearly no difference was observed between 180°C

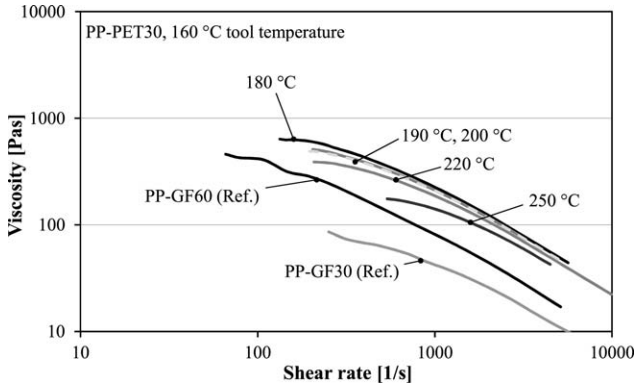


**Figure 4.** Viscosity in relation to shear rate of polyester reinforced polypropylene.

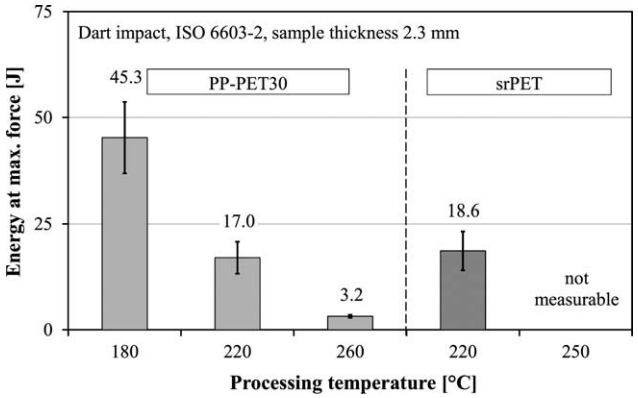


**Figure 6.** Drop impact energy obtained from samples from the compressed sheets.

to 220°C. Because of the very low viscosity observed at the temperature of 250°C, it was assumed that the PET fibers might have been damaged during the heating process.

The viscosity of the srPET system was recorded to be significantly higher than the PP-PET30 material combination (Figure 5). The minimum processible temperature of 220°C demonstrated a viscosity in the range of 10,000 Pas, which was 10 times higher than the PP-PET30. Only the low viscous, honey-like state at 260°C, in which significant fiber damage was expected, revealed a viscosity in the range of the PP-PET30 model compound.

By concluding from the rheometry results, a significantly better flow processability in complex molds was expected from the PP-PET30. Despite this, both compounds could be well handled and processed by means of the used standard extrusion equipment.

### Manufacturing of Sheets and Mechanical Testing

After the rheological data had been obtained, a shear edge mold for the manufacturing of sheets was applied on the press. Several sheets were manufactured at distinct extrudate temperatures to investigate the influence of temperature on the mechanical performance of the SRP. Specimens were cut from the manufactured sheets.

The dart impact resistance decreased for both material combinations with increasing process temperature (Figure 6). Although the sample of the srPET manufactured at 260°C did not deliver a measurable result, the sample behavior itself revealed a very weak condition though. The srPET sheets had a transparent, glassy morphology, which was so brittle that the forces during the impact test were not high enough to exceed the random noise of the load cell. As a consequence, no measurable result could be recorded. The PP-PET30 indicated the expected behavior of higher extrudate temperatures resulting in increased fiber damage and, thus, in lower impact resistance. This assumption could be additionally validated with notched Charpy impact samples (Figure 7). In Charpy tests, the polymer reinforced composites could be observed losing significantly their mechanical performance when they were previously processed at a higher temperature. This result indicated that the PET fibers lose their reinforcing effect and thus their integrity. By concluding from the impact results for PP-PET, the lowest extrudate temperature of 180°C should be applied for processing, whereas the corresponding process temperature for srPET should not be higher than 220°C. If this process strategy was pursued, the PP-PET compound even exceeded significantly the impact properties of 30 wt-% glass fiber reinforced PP. This behavior is attributed to the high ductility of the polymer fibers

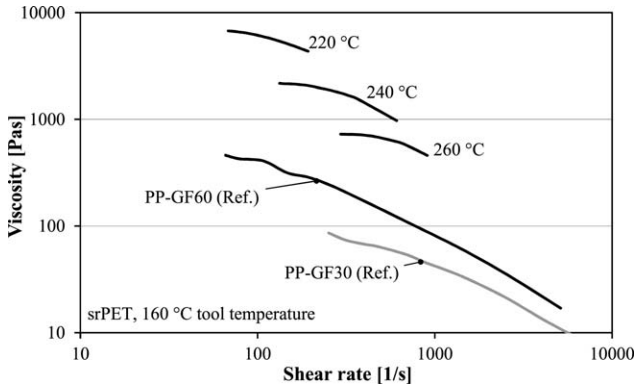


**Figure 5.** Viscosity in relation to shear rate of extruded all-polyester pellets.

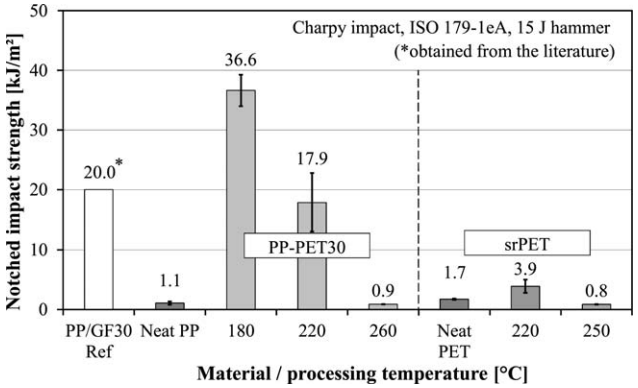


**Figure 7.** Results of notched Charpy impact tests in relation to process temperature.

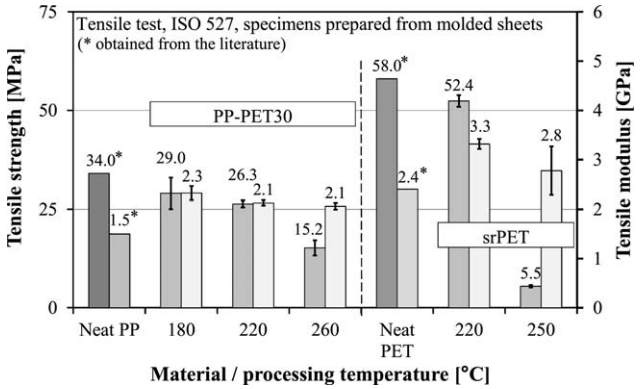


**Figure 8.** Tensile strength in comparison to manufacturing temperature for PP-PET30 and self-reinforced PET.

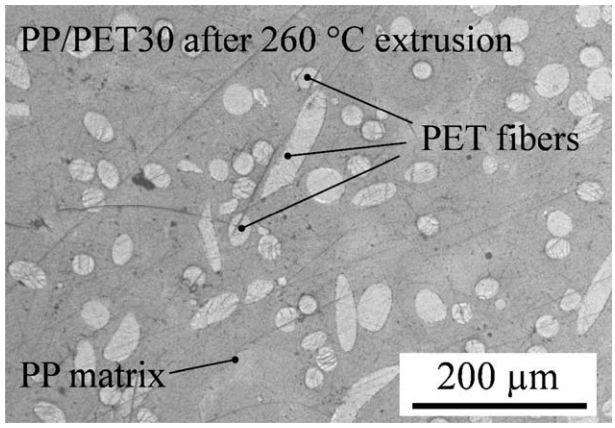


**Figure 9.** Light microscopic image of a PP-PET30 sample processed at 260°C.

in comparison to the glass reference. However, the srPET resulted in very poor impact properties.

Analogue trends in comparison to the results of the impact tests were obtained from the tensile tests (Figure 8). The highest performance was measured from samples with the lowest feasible extrudate temperature during processing. This conclusion is valid for PP-PET30 as well as for srPET. The tensile experiments revealed a significant higher tensile strength and modulus for the srPET compounds than for the PP-PET30. However, it should be noted that the tensile strength was found to be lower than that of the reference values taken from the literature for neat materials. In contrast, the modulus was in both cases slightly higher than the neat reference materials. Moreover, the strain at maximum force was in the case of using a feasible process temperature with limited fiber damage significantly higher for the PP-PET30 (13.1% at 180°C) than for the srPET (2.0% at 220°C). For both materials, the strain decreased with increasing temperature as observed with the strength and the modulus.

As a general rule and conclusion from the experimental series, the lowest possible process temperature should be applied to preserve the reinforcement integrity. This result conforms to the conclusions of Chen et al.[25] who stated that a low holding time and low temperature lead to the highest tensile properties for srPET. The mechanical deterioration with increasing processing temperature affects the impact resistance significantly more than the tensile strength. The reason can be explained by a reduction of the fiber length that has a higher effect on the impact than on the tensile properties.[26] A microscopic analysis was performed to verify this theory. In these images the polypropylene matrix could be clearly distinguished from the polyethylene terephthalate even after using a process temperature exceeding the melting temperature of the reinforcement (Figure 9). This observation can be explained by the immiscibility of PP and PET. As the resolution of the microscopy was too small, the change of losing the fibrous state and the fiber length could not be clearly observed for the PP-PET30. In contrast, the cross section of an overheated srPET revealed a homogeneous morphology. Matrix and fibers could not be distinguished from each other after processing at elevated temperatures, which is a proof for the melting of the reinforcing fiber. At lower temperatures, however, the two phases could still be clearly distinguished from each other as indicated by Figure 10.

### Manufacturing of Complex Shaped Demonstrators

The applied demonstrator mold was a Y-shape geometry containing several ribbings for examining the flow performance of the extrudate (Figure 11). For a complete mold filling, a mass of 1 kg was calculated for PP-PET30, whereas 1.3 kg was needed for srPET. The mold was preheated to 90–100°C when the extrudate was placed in front of the cavity on the lower mold part.

For improving the material flowability, PP-PET30 was used at a temperature of 195–200°C. As the mold filling was executed in

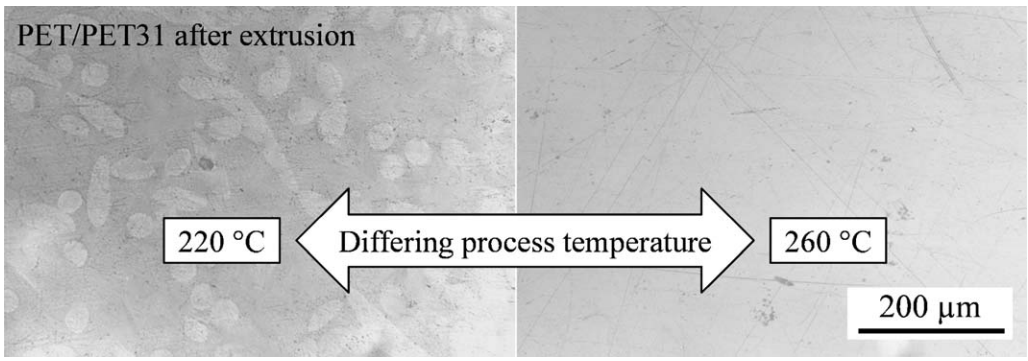


**Figure 10.** Microscopic image of an all-polyester composite processed at 220°C in comparison to one processed at 260°C.

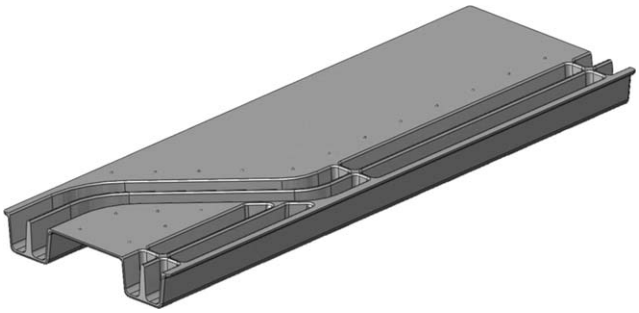

**Figure 11.** CAD drawing of the applied Y-shaped demonstrator part.

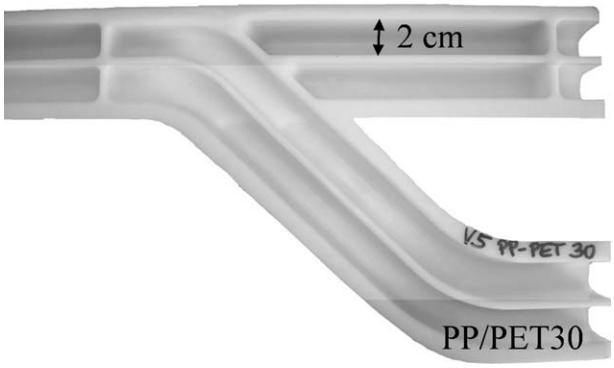


**Figure 12.** Complete filling of a complex-shaped mold with PP-PET30.

a semi-continuous concept, because of the larger amount of molten material, a higher temperature than previously measured for the best rheological and mechanical performance was necessary to compensate thermal losses. Although a higher temperature was used, the processability was unproblematic with PP-PET30—the mold could be completely filled without voids resulting in a good demonstrator surface quality and intact fibers (Figure 12).

In contrast to the PP-PET30 model system, the processing of the self-reinforced polyester was challenging and less successful. The high viscosity led to an incomplete mold filling, which resulted in frozen melt flow fronts and voids within the demonstrator (Figure 13). The material also revealed extreme shrinkage, which made a deforming nearly impossible. By increasing

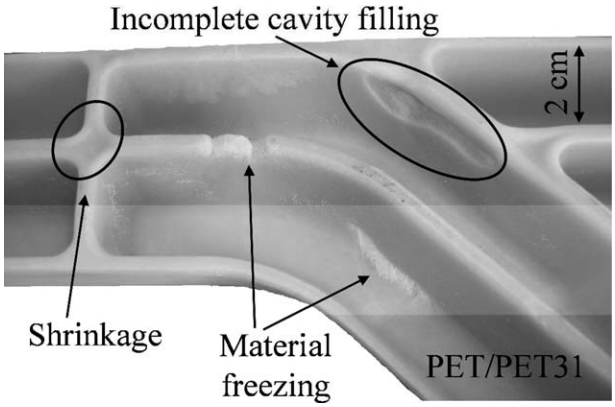


**Figure 13.** Observed challenges with srPET pellets in a LFT process.

the mold temperature from 60°C to 80°C, the flowability and deformability were improved. Yet, the material temperature at the end of the molding cycle remained higher than the glass transition temperature, which caused warpage. As a consequence, the developed srPET system is assumed to be predestined and more efficient with less complex molds because of the lower flowability of the material.

## CONCLUSION

It was demonstrated that the processing of newly developed polymer-reinforced thermoplastic pellets in a LFT compression molding process chain is feasible without the application of special heating methods. The PP-PET material system revealed good rheological properties for compression molding resulting in a well-processed demonstrator. The viscosity of the material was low enough to enable the filling of complex cavities. The self-reinforced polyester demonstrated higher mechanical properties than the investigated PP-PET30 system but resulted also in a higher viscosity and a higher sensitivity to overheating. The viscosity was measured in the range of 10,000 Pas and did not allow a sufficient flow processing within the applied complex mold. Despite this, the filling of sheet-like molds was still feasible.

By concluding from the obtained results, the extrudate temperature of self-reinforced materials has to be chosen to a minimum to preserve the performance of the polymeric reinforcement. Nevertheless, a compromise has to be made as a lower extrudate temperature simultaneously causes a higher viscosity that limits the application of the respective material within complex tools. Although intrinsic heating methods are not essential for the processing of the materials applied in this study, they still could improve the heating homogeneity and reduce the thermal impact on the meltable reinforcement.

## ACKNOWLEDGMENTS

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