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Influence of the Processing Temperature in the Calendaring Process of Staple Fiber Yarns on the Degree of Consolidation and the Thermal Properties

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Influence of the Processing Temperature in the Calendaring Process of Staple Fiber Yarns on the Degree of Consolidation and the Thermal Properties

Martin Detzel, Peter Mitschang and Ulf Breuer[1]

Abstract: In this study, carbon/polyamide 6 staple fiber yarns were heated above the melting temperature of the polymer in a modified impregnation and calendaring process using two hot air blowers, stretched to align the fibers in the yarns, and formed into tapes. Tapes were produced at different process temperatures and the influences on the degree of consolidation and the thermal properties of the tapes were characterized. While improved impregnation quality can be achieved at higher temperatures, a decrease in the crystallization peak temperature of the impregnated tape was observed, indicating thermal degradation.

Keywords: Recycled Carbon Fiber, Thermal Properties, Staple Fiber Yarn, Tape Manufacturing

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Introduction

Depending on the manufacturing process, during the production of carbon fiber reinforced polymers approximately 40% of carbon fibers become waste, even though they are high-quality production offcuts [1]. Due to their high manufacturing costs and energy requirements, it is worthwhile to use these fibers in components with the highest possible fiber orientation. One way of using recycled carbon fibers (rCF) in an automated and conventional composite processing method is through the production of rCF tapes. For short rCF in the range of 1-12 mm, it is possible to produce rCF tapes using a wet-laid process [2,3], while textile processes can be used for fibers longer than 25 mm [4-6]. In textile processes, either slivers [7] or yarns [4,8] are produced, to which thermoplastic fibers are added as a manufacturing aid and for subsequent fiber impregnation. Depending on the weight amount of thermoplastic fibers in the textile intermediate, thermally stabilized or fully consolidated tapes can be produced by melting the polymer. During the tape production process, the polymer must be in a fully molten state until consolidation but should not be heated above the degradation onset temperature of the polymer. The aim of this study was to determine the material temperature during processing in the tape production line as a function of the fixed hot air blower temperature and to investigate the resulting degree of consolidation and the thermal properties of the produced tape.

Experimentation

Material

Staple fiber yarns with a content of 60 wt.-% CF staple fibers and 40 wt.-% PA6 staple fibers were produced with a titer of 500 tex by Wagenfelder Spinnerei GmbH, using the wrap spinning process. To ensure the stability of the yarn, a PA6 wrapping filament was used, a different PA6 type than the PA6 staple fibers due to its processability. Winding the staple fiber yarns with the wrapping filament leads to the undulation of the yarn and thus to misalignment of the fibers. The utilized rCF fibers are of the Panex® type 35 from the manufacturer Zoltek (St. Louis, MO, USA), which are spool remnants cut to a length of 80 mm for the spinning process. An image of an rCF staple fiber yarn spool and a microscopic image showing the components are presented in Figure 1.

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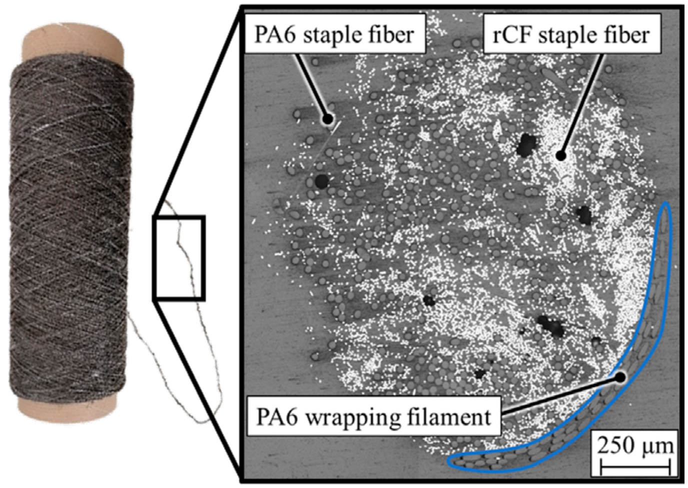

Figure 1. Spool with staple fiber yarn and microscopy image of the staple fiber yarn (PA6 wrapping filament highlighted in blue).

Determination of the Process Window and the Thermal Properties of the Produced Tapes

To determine the process window, both differential scanning calorimetry (DSC) to measure the melting point in the first heating cycle and thermogravimetric analysis (TGA) to detect the degradation onset temperature for the two PA6 types were conducted. The thermal properties (peak melting and recrystallization peak temperatures) of the produced tapes were determined using DSC in the second heating cycle and the cooling cycle. In both DSC heating cycles, the samples were heated from 20°C to 280°C under a nitrogen flow of 30.0 mL/min at a heating rate of 10 K/min. The cooling cycle from 280°C to 20°C, was carried out under a nitrogen flow of 30.0 mL/min at a cooling rate of -10 K/min. The TGA was conducted under an airflow of 30.0 mL/min in the temperature range of 30-520°C at a heating rate of 10 K/min.

Tape Production

Tape production can be described as a modified calendaring and impregnation process and was carried out on the tape production line shown in Figure 2.

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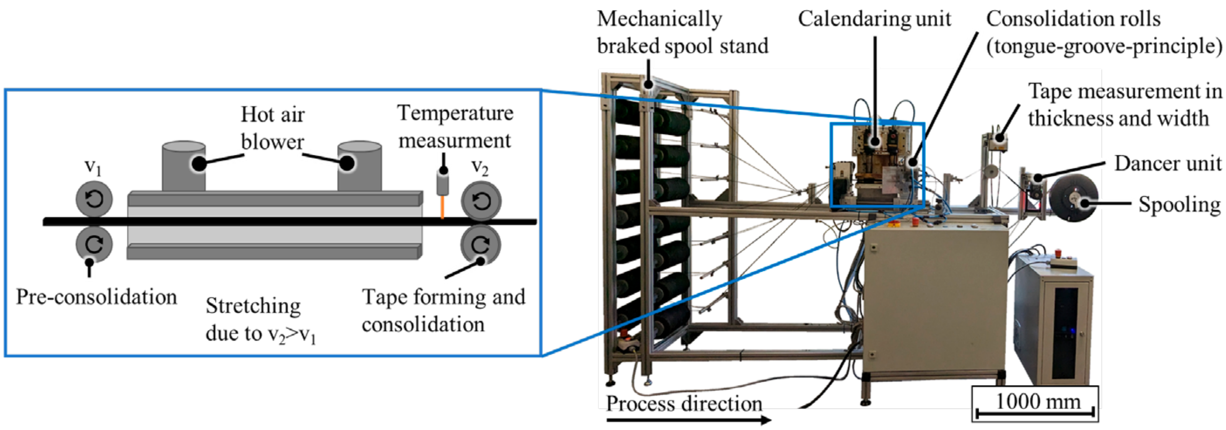

Figure 2. Tape production line with a schematic illustration of the calendaring process.

14 spools of yarn are used to produce a 12.7 mm wide tape. These are stored in a mechanically braked spool stand and pulled into the calendaring unit by the pre consolidation rollers. In the 250 mm long heating zone of the calendaring unit, the yarns are heated above the melting temperature of the polymer by two adjustable hot air blowers. The yarns are stretched by the speed difference (stretching factor) between the consolidation rollers and the pre-consolidation rollers, which leads to an alignment of the rCF in the process direction.

Table 1. Temperature, speed and stretching factor used in tape production.

Parameter set	Temperature in °C (Hot air blower) Pass 1 / Pass 2	Speed v_1 in m/min Pass 1 / Pass 2	Stretching factor $v_2>v_1$ Pass 1 / Pass 2
450°C (Pass 1) / (Pass 2)	450 / 450	1.4 / 1.1	1.1 / 1.09
475°C (Pass 1) / (Pass 2)	475 / 475	1.4 / 1.1	1.1 / 1.09
500°C (Pass 1) / (Pass 2)	500 / 500	1.4 / 1.1	1.1 / 1.09
525°C (Pass 1) / (Pass 2)	525 / 525	1.4 / 1.1	1.1 / 1.09
550°C (Pass 1) / (Pass 2)	550 / 550	1.4 / 1.1	1.1 / 1.09

The actively cooled consolidation rollers work on the tongue-and-groove principle and form a 12.7 mm wide tape from the yarns. The consolidation force was applied by a pneumatic cylinder and set to 120 N. Following consolidation, the produced tape was geometrically measured using a laser profile sensor and then wound onto Häfner spools. Further information on the production process can be found in [8], which describes that a second pass through the tape production line had a positive effect on fiber orientation and mechanical properties compared to tapes produced with the identical stretching factor in a single pass. Therefore, in this parameter study, all tapes were produced with a second pass at the same speeds and stretching factor. Only the hot air blower temperature was varied in increments of 25 K within the range of 450-550°C. The parameter sets are listed in Table 1 and abbreviated in the subsequent figures according to the hot air blower temperature used.

Determination of the Material Temperature During Processing

The temperature in the middle of the material during production was determined by in-situ temperature measurements. For this purpose, a type K thermocouple was inserted into a yarn, fixed and processed with the parameters listed in Table 1 for the first pass through the tape production line. To determine the temperature during the second pass, tapes were previously produced with the parameters for the first pass, then a type K thermocouple was inserted, fixed, and processed with the second pass parameters. To ensure statistical reliability, ten repetitions were carried out.

Determination of the Degree of Consolidation

The degree of consolidation was assessed by determining the void volume content using microscopic images. Five tapes per parameter level were tested for both the first and second pass through the tape production line. The void volume content was determined at three positions of the tapes: left, middle, and right. It was automatically evaluated using the gray value analysis.

Results

Determination of the Process Window

Figure 3(a) shows the DSC results of the first heating cycle for the two PA6 types. There is no significant difference between the two PA6 types. The peak melting temperature for the PA6 staple fiber is 219.7°C, while for the PA6 wrapping filament it is 219.9°C. Both melting temperatures are within the expected range for PA6. Figure 3(b) shows the results of the TGA, which reveal a clear difference in the degradation behavior of the two PA6 types. The first degradation onset temperature of the PA6 staple fiber is 320°C, while for the PA6 wrapping filament it is 380°C. The lower degradation onset temperature of the PA6 staple fibers may be attributed to additives present in the polymer. A process window of 220°C to 320°C was derived from this peak melting temperature and the onset of degradation temperature.

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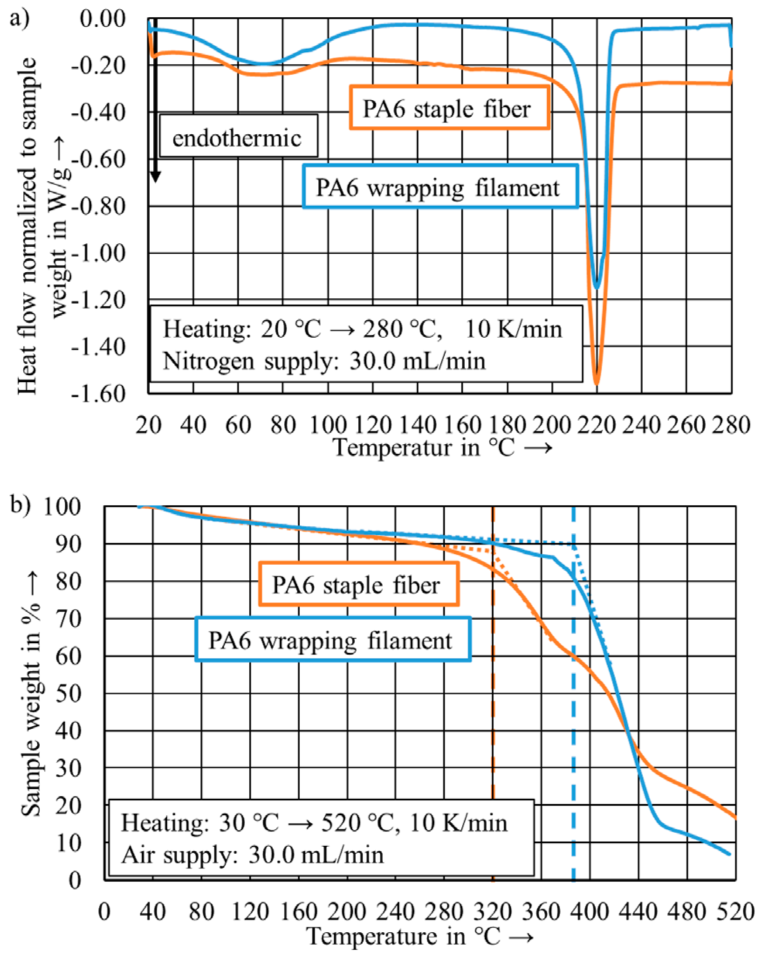

Figure 3. (a) DSC-thermogram of the PA6 staple fiber and the PA6 wrapping filament and (b) TGA-thermogram of the PA6 staple fiber and the PA6 wrapping filament.

Determination of the Material Temperature During Processing

Figure 4(a) shows the temperatures in the center of the yarn for the hot air blower temperatures ranging from 450 to 550°C for the first pass through the tape production line. The increase in yarn temperature immediately after leaving the pre-consolidation rollers is due to the hot air exiting the heating zone. Upon entering the heating zone, the yarns quickly heat up above the melting temperature of the PA6. The passage of the first hot air blower is clearly indicated by a change in the temperature gradient. The maximum temperature in the material is reached at the second hot air blower. The material temperature decreases slightly until it reaches the consolidation rollers. During the consolidation process, the material temperature is rapidly lowered to about 100°C by the actively cooled consolidation rollers. The subsequent slow cooling occurs passively through ambient temperature. For the set hot air blower temperatures of 525°C and 550°C, the degradation onset temperature of the PA6 staple fiber in the center of the yarn is exceeded. Taking into account

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the standard deviation of the experiments, the degradation onset temperature is also reached in some experiments with a hot air blower temperature of 500°C. Figure 4(b) shows the temperatures for the second pass through the tape production line for previously produced tapes. A comparable heating behavior to that of the yarns (Figure 5[a]) is observed. Due to the lower processing speed, the dwell time of the tapes in the heating zone is longer; but the degradation onset temperature in the center of the tape is not reached for any of the set hot air blower temperatures. The more open structure of the yarns allows faster heating of the sample's center. A statement about the temperature at the sample surface cannot be provided at this time but should be measured in future studies.

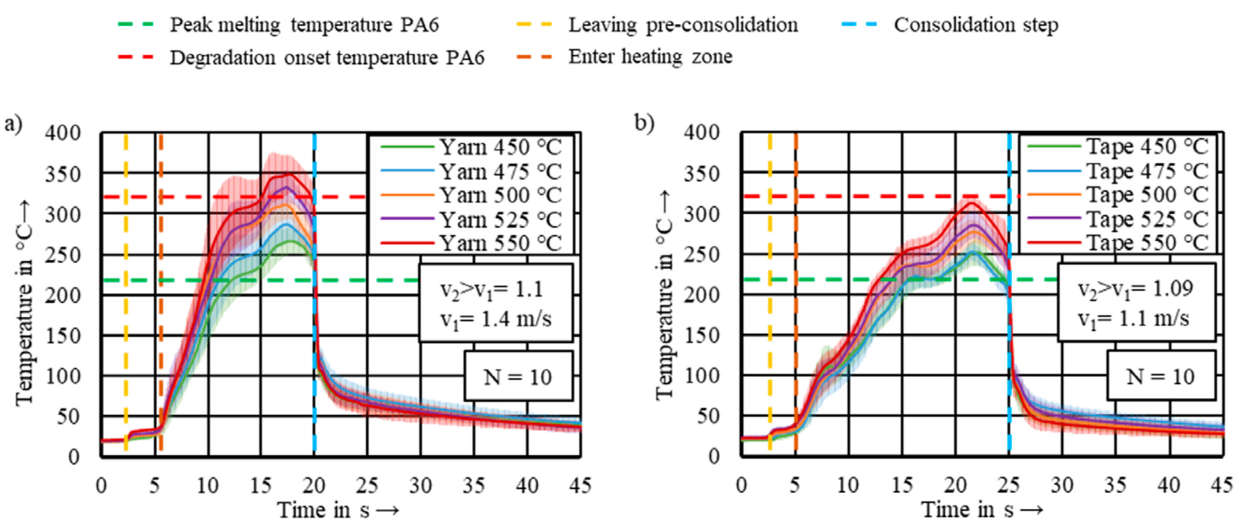

Figure 4. (a) Temperature in the center of the staple fiber yarn during the first and (b) temperature in the center of previously produced tape during the second pass through the tape production line.

Determination of the Degree of Consolidation

Figure 5 shows the results of the void volume analysis to evaluate the degree of consolidation. The results are divided into the first and second system runs. In some microscopy images for temperatures 450°C and 475°C, unmelted PA6 fibers can be observed at the edges of the tape after the first pass through the tape production line, see Figure 5(b). Except for the temperature of 450°C, higher temperatures during the first pass result in lower void volume content. At 475°C, the void volume content is 7.3%; increasing the temperature to 550°C reduces the void volume content to 2.6%. The low void volume content at 450°C (2.2%) is due to a poorly consolidated tape surface, which led to post-impregnation with embedding material, see Figure 5(c).

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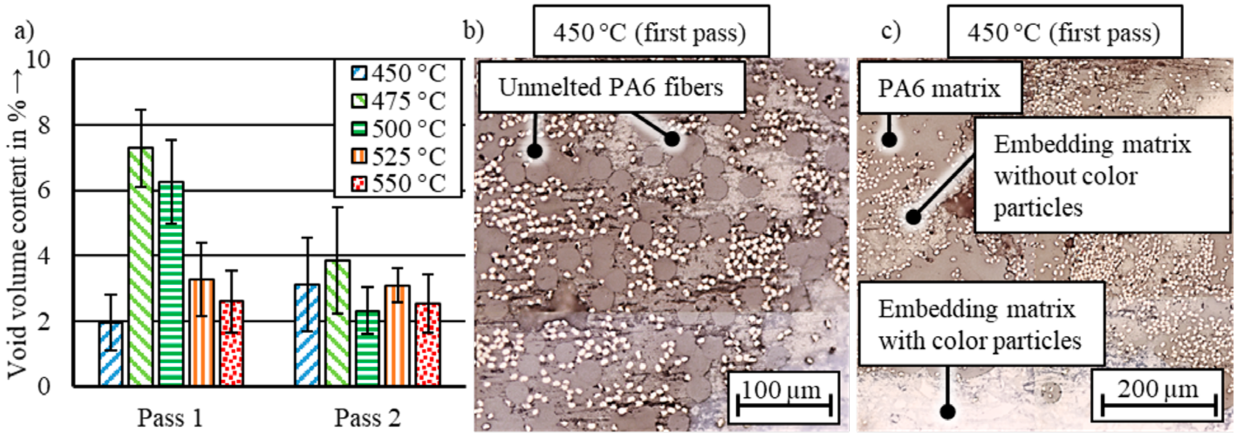

Figure 5. (a) Void volume content after the first and second pass for different hot air blower temperatures, (b) unmelted PA6 fibers at the edge of produced tapes at 450°C after the first pass and (c) tape produced at 450°C after the first pass with post-impregnation of embedding material.

These areas could not be detected as voids by the automatic evaluation. For future research, compression thermal analysis [9] should be used to measure the degree of consolidation, as this method can evaluate samples without a closed surface. The results of the tapes after the second pass through the tape production line show no clear influence of the hot air blower temperature. The void volume content decreases after the second pass through the equipment and ranges from 2.3% to 3.8%.

Determination of the Thermal Properties of the Produced Tapes

The results of the DSC measurements are shown in Figure 6 for the hot air blower temperature used during tape production. Compared to the PA6 wrapping filament and the PA6 staple fiber, the peak melting temperature of the tapes decreases regardless of the selected hot air blower temperature. The peak melting temperature of the produced tapes ranges from 214.2°C to 216.8°C, while the PA6 wrapping filament is at 219.9°C and the PA6 staple fiber at 221.5°C. At temperatures of 450°C and 475°C, the crystallization peak temperature of 188.5°C and 188.6°C is in the range between PA6 staple fiber 186.1°C and PA6 wrapping filament 193.5°C. A decrease in the crystallization peak temperature is observed, starting from a hot air blower temperature of 500°C. For 500°C and 525°C, the crystallization peak temperature is 184.4°C. Increasing the temperature to 550°C leads to a drop in the crystallization peak temperature (182.6°C). A change in the crystallization peak temperature can be attributed to a change in molecular weight due to thermal degradation [10].

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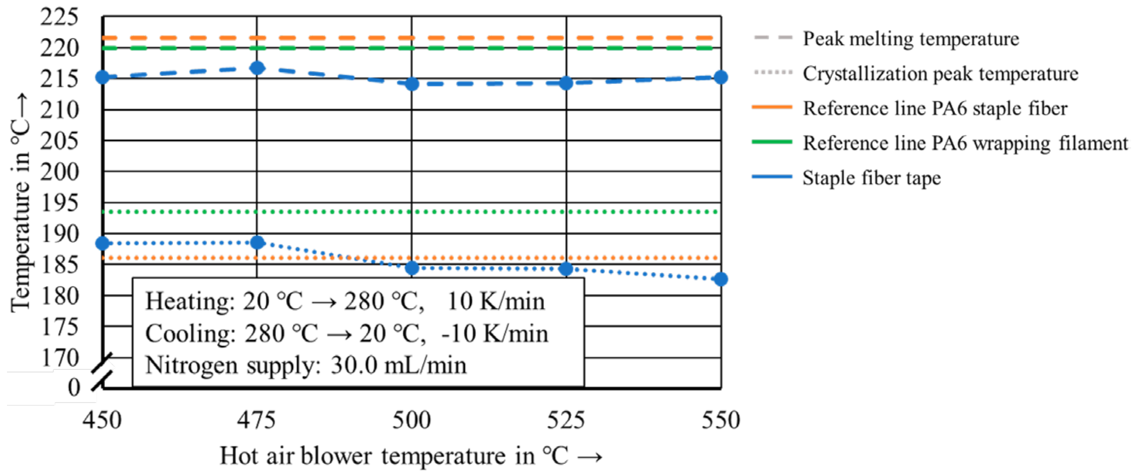

Figure 6. Influence of hot air blower temperature on peak melting and crystallization peak temperature.

Conclusion

By combining the results of the DSC and TGA tests, the processing window for the staple fiber yarns was determined. The subsequent in-situ temperature measurements showed that hot air blower temperatures above 500°C led to material temperatures exceeding the degradation onset temperature of the PA6 staple fibers. Exceeding the degradation onset temperature in these experiments may have contributed to the observed decrease in the crystallization peak temperature. However, these higher temperatures resulted in the lowest void volume contents after the first pass. Improved consolidation was achieved without noticeable influence from the hot air blower temperature after the second pass. For the future production of SF tapes, a processing temperature of 450°C or 475°C should be selected at the utilized processing speed to prevent thermal damage while ensuring good material consolidation.

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