

TENCEL® FIBER REINFORCED PLA COMPOSITES

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Summary: Two PLA grades by Natureworks LLC were reinforced with man-made regenerated cellulose fibers Tencel® FCP by Lenzing AG to generate 100 % biocomposites. Ingeo 3251 D is a standard injection molding (IM) PLA type, while 3260 HP is modified for accelerated crystallization with a bio-based lubricant. Compounding was performed on a parallel, co-rotating twin screw extruder Brabender DSE20. Specimens were prepared on a Wittmann-Battenfeld HM 1300/350 IM machine. The composites prepared were characterized by DSC measurements, and tested for mechanical properties (tensile, impact, HDT). The results show that FCP acts as a nucleating agent, and allows a reduction of IM cycle times. Ingeo 3260 HP is able to crystallize in its presence when cooled from the melt at 10 K/min. Based on a more than 75 % amorphous PLA matrix, Young's modulus and impact strength can be improved significantly by reinforcement with Tencel® FCP. Increasing crystallinity (X_c) by increasing IM tool temperature leads to a dramatic increase in impact performance for the neat polymer. Based on this matrix with X_c values above 50 %, Young's modulus and HDT-A can be enhanced by reinforcement with FCP.

1 INTRODUCTION

Today, Poly(lactic acid) (PLA) is the most commercially relevant bio-based polymer. Its production volume was 180 kt in 2012, and is forecast to rise to over 800 kt by 2020 [1]. Up to now, PLA is mainly replacing commodity polymers in packaging, and is also used in novel biomedical applications [2]. Due to its relatively high modulus and ultimate strength, this polymer is also promising for technical applications. However, low impact strength and heat deflection temperature (HDT) still limit its application range. Furthermore, slow crystallization interferes with the high cooling rates typical for industrial polymer processing operations, particularly injection molding. Today, the processing-related issues and low impact performance are mostly remedied by blending PLA with bio-polyesters or starch-based polymers [3]. Thereby, however, the potential for high stiffness and strength values is compromised to a large extent.

To overcome this drawback, one way is reinforcement with fibers. Of course, employing conventional fibers like glass or carbon fibers defeats the purpose of a bio-based polymer. Thus, fibers from renewable sources would be the logical choice for PLA reinforcement,

yielding a 100 % bio-composite. There is already a lot of scientific literature available on such composites [4-6]. However, the results presented often fall behind expectations based on constituent properties, because efficient reinforcement needs both good fiber/matrix interaction and (partial) crystallization (if heat deflection properties should be improved, as well). Furthermore, typical natural fibers like hemp or flax have well known disadvantages like seasonal change of quality, emission of odorous compounds, and problematic processing. Man-made cellulose fibers produced from wood, like Tencel® by Lenzing AG, avoid these issues [7]. Thus, the focus of this research was the production of PLA-Tencel® composites, and the exploration and optimization of their property profile.

2 MATERIALS AND METHODS

2.1 Materials

Two PLA grades by *Natureworks LLC* were employed as matrix polymers in this study (Table 1). They were chosen based on their high flowability. Both have a density of 1.24 g/cm³. The main difference between the two grades is that Ingeo 3260 HP contains the bio-based lubricant LAK-301 by *Takemoto*, which is meant to accelerate crystallization.

Table 1: PLA grades used in this study.

Name	Code	MFR _{210°C/2.16 kg} [g/10 min]	Description
Ingeo 3251 D	D	85	-
Ingeo 3260 HP	HP	60	cont. 1 wt% of lubricant

As reinforcement fiber, Tencel® FCP 10/300/M by *Lenzing AG* was used. This is a man-made regenerated cellulose fiber based on wood, which is produced by a Lyocell process. It has a density of 1.50 g/cm³, and the initial length and diameter are ~300 µm and 10 µm, respectively. The fiber carries a specific surface treatment which allows for dosability.

2.2 Methods

Both polymers and fibers were dried to constant weight at 80°C before processing. A parallel, co-rotating twin screw extruder *Brabender DSE20*, coupled to an *ECON EUP50* under-water pelletizer (UP), was used for compounding. The DSE20 has a screw diameter of 20 mm, and a length of 40 d. A revolution speed of 350 rpm, and a throughput of 8 kg/h was maintained for all trials. The temperature profile used is shown in Table 2, and lead to melt temperatures between 202 – 209°C, being directly proportional to FCP content. The polymers were fed through the hopper, while the fibers were fed via a sidefeeder mounted between HZ1 and HZ2.

Table 2: Temperature profile used for PLA compounding. PW, DP and SV represent the process water, the die plate and the starting valve of the UP, respectively. The zone under the hopper before HZ1 is water-cooled.

Zone	PW	DP	SV	HZ7	HZ6	HZ5	HZ4	HZ3	HZ2	HZ1
Temp. [°C]	60	180	180	180	180	190	190	190	210	220

Table 3: Compounds prepared on the DSE20.

Comp. Nr. / Code Material [wt%]	-01 / D10	-02 / D20	-03 / D30	-04 / HP10	-05 / HP20	-06 / HP30
Ingeo 3251 D	90	80	70	0	0	0
Ingeo 3260 HP	0	0	0	90	80	70
FCP 10/300/M	10	20	30	10	20	30
Fiber content [v%]	8.5	17.3	26.3	8.5	17.3	26.3

The melt flow rate (MFR) of the compounds prepared was measured at 190°C and under a load of 5.0 kg, employing a *Zwick 4105* equipment and following ISO 1133.

Specimens of ISO 527-2 1A specified dimensions were prepared on a *Wittmann-Battenfeld HM 1300/350* injection molding (IM) machine. Before IM, all compounds were dried to constant weight at 80°C, if necessary. The temperature profile employed is shown in Table 3. The standard tool temperature was 25°C. Some compounds were also processed with a tool temperature of 120°C to achieve crystallization in the mold (indexed with _c). A constant injection speed of 50 cm³/s was run. Packing pressure was held at 25 % of the maximum injection pressure for 10 s, while total cooling time was varied depending on formulation and tool temperature.

Table 4: Temperature settings on the injection molding machine.

Zone	Tool	Nozzle	Zone 1	Zone 2	Zone 3	Feeder
Temp. [°C]	60	190	185	180	175	50

All specimens were conditioned in a climate cabinet at 23°C / 50% relative humidity for one week before testing.

Density of the composites was determined by a buoyancy method, employing a *Sartorius* analytical scale, and following ISO 1183-1. Volumetric filler contents were calculated from the densities of the components as given under *Methods*.

Tensile properties were tested according to ISO 527. Modulus was determined at 1 mm/min, while strength was determined at 5 mm/min. Six specimens each were employed for tensile testing.

Charpy impact strength was determined according to ISO 179. Ten specimens each were measured notched (1eA) and unnotched (1eU) at 23°C (room temperature).

Heat deflection temperature was determined according to ISO 75, employing mode A (HDT-A; 1,8 MPa). Three specimens each were used per sample.

For DSC measurements, a *TA Instruments Q20* was employed. Cyclic up-down-up runs were performed from room temperature to 220°C, with a rate of 10 K/min. Crystallinity (X_c) values in [%] were calculated from first heating run data, in order to reflect the actual state of the specimens as used for mechanical testing. The cold crystallization enthalpy was subtracted from the melting enthalpy, and then corrected for filler content. A value of 93.7 J/g was taken as the theoretical melting enthalpy of 100 % crystalline PLA [8].

3 RESULTS AND DISCUSSION

3.1 Processing and Thermal Properties

In each injection molding trial, it was attempted to reduce the cooling time to the acceptable minimum for part ejection. Cooling time of course controls cycle time, which is shown in Figure 1 as a function of material processed and tool temperature. At 25°C, introducing FCP as reinforcement leads to a significant reduction in cycle time for both matrix polymers. However, increasing the FCP content from 10 to 30 wt% does not have a significant effect. This is probably because, as will be shown below, FCP has some nucleating effect in PLA. At the low tool temperature of 25°C, however, rapid cooling prevents crystallization to a large extent. Thus, the nucleating effect of the fiber plays only a minor role, and mostly amorphous parts are produced.

At a tool temperature of 120°C, the situation is quite different. Only formulations based on the “accelerated crystallization” type Ingeo 3260 HP were processed at this temperature. Preliminary trials had shown that it was practically impossible to obtain specimens from the unmodified Ingeo 3251 D under these conditions. Obviously, also with neat HP, with a tool temperature of 120°C the cycle time is far too long for industrial production. However, as will be shown below, this allows for the preparation of specimens with significantly higher X_c values. When introducing FCP, cycle time is reduced by 5 times. This is because at the higher tool temperature, the nucleating potential of the fibers can be realized to a by far larger extent. Leading to accelerated solidification, this allows for quicker part ejection, if not leading to higher overall X_c values (Table 5).

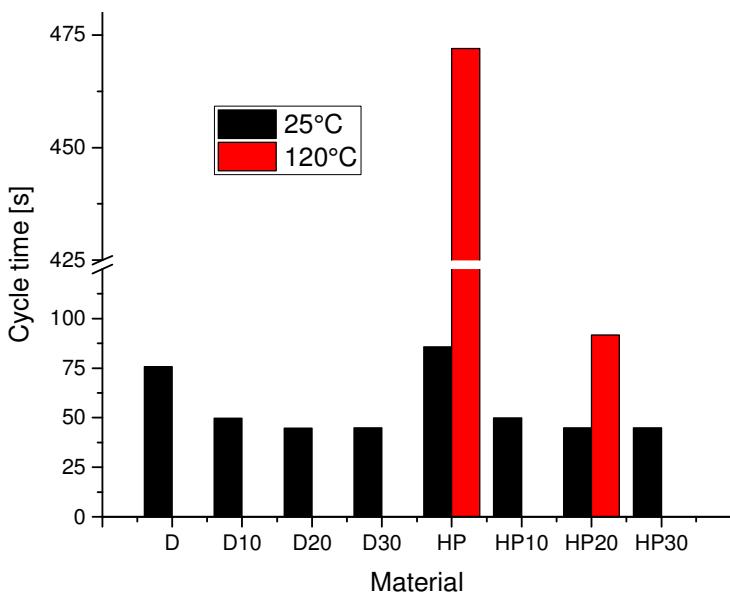


Figure 1: Injection molding cycle times for the different materials investigated in this study.

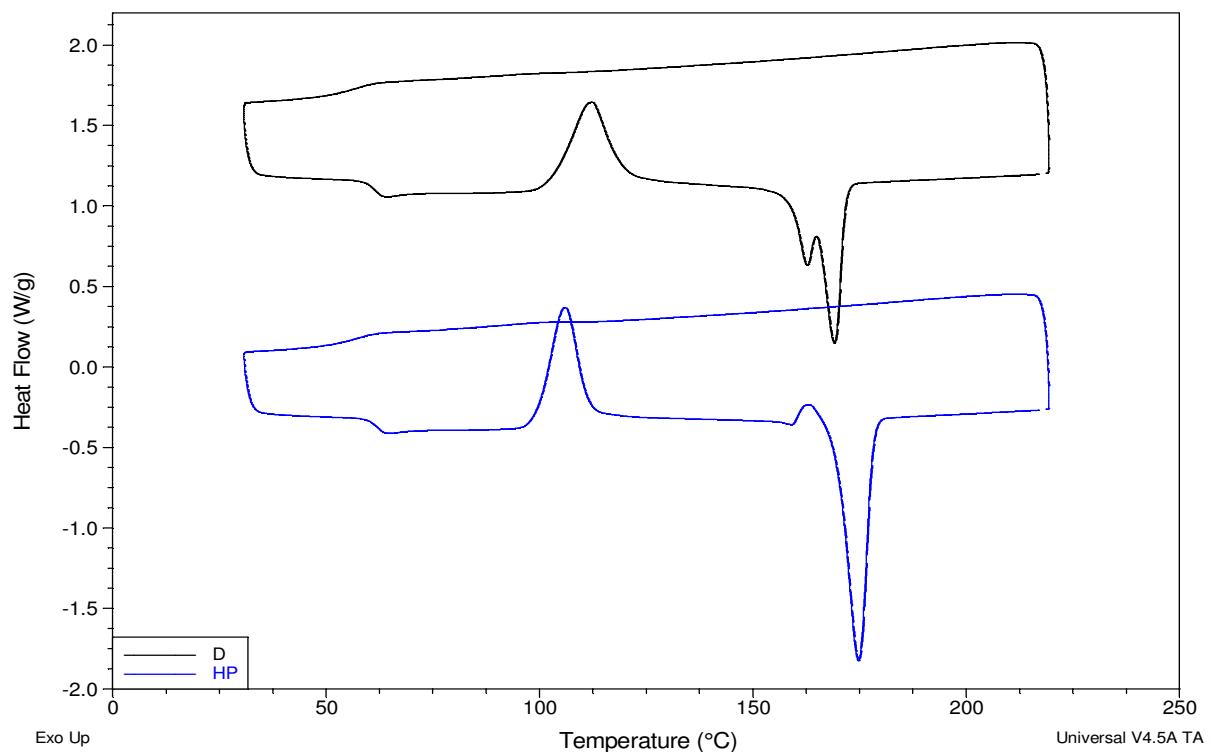


Figure 2: DSC cooling and 2nd heating curves for Ingeo 3251 D (black) and 3260 HP (blue). 1st heating is not shown because it is almost identical to 2nd heating. Samples were prepared from specimens injection molded with a tool temperature of 25°C.

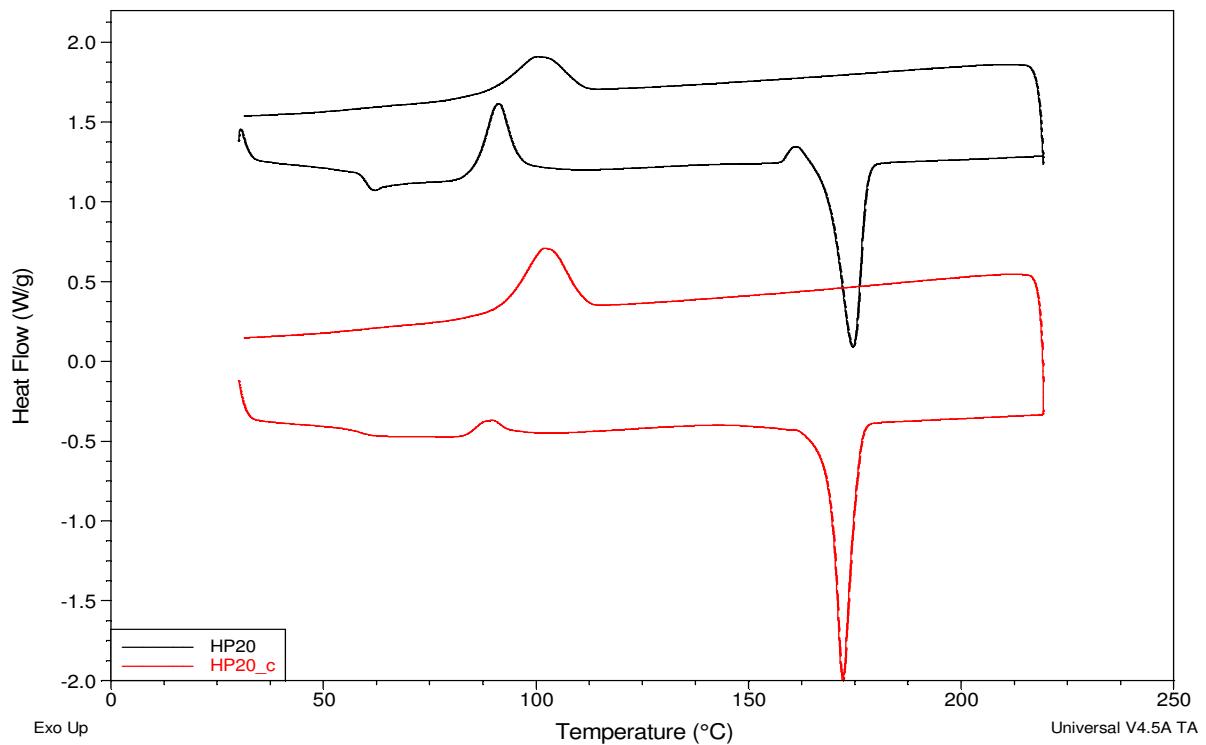


Figure 3: DSC 1st heating and cooling curves for HP20 (black; 25°C) and HP20_c (red; 120°C). 2nd heating is not shown because it is almost identical to 1st heating for HP20.

As Figure 2 shows, the two PLA types used are significantly different in terms of their thermal properties. Both polymers do not show a crystallization peak during cooling with 10 K/min. This is because this process is so slow in PLA that it is almost inhibited under these conditions. In injection molding with a tool temperature of 25°C, cooling rates are in fact dramatically higher. Both PLA types show comparable cold crystallization peaks at 90 – 120°C, while their melting peaks look different. Ingeo 3251 D shows a double, while 3260 HP shows just a single one. The former indicates incomplete crystallization, resulting in smaller spherulites with lower melting temperatures [9]. For Ingeo 3260 HP, the enhancement of chain mobility by lubricant modification probably allows the formation of more stable crystalline structures.

Injection molding tool temperature has a significant effect on crystalline morphology, also (Figure 3). Samples from specimens injection molded with a tool temperature of 25°C (HP20) show a distinct cold crystallization peak in the first heating run. For those prepared at 120°C (HP20_c), on the other hand, this feature is less pronounced, indicating that to a large extent, crystallization has already taken place during the process. The cooling runs look quite similar for both samples. In contrast to HP in Figure 2, there is a distinct crystallization peak during cooling. This means that the FCP fibers have some nucleating effect, which can at least partly be realized during cooling from the melt at 10 K/min.

Table 5: Crystallinity of PLA and some of its composites as calculated from DSC data.

Code	D	D20	HP	HP20	HP_c	HP20_c
Tool temp. [°C]	25	25	25	25	120	120
X _c [%]	6.9	17.2	18.7	24.2	64.7	55.1

Table 5 clearly shows the effect of formulation and tool temperature on the X_c values of PLA and some of its composites. As determined from injection molded specimens, the neat, unmodified Ingeo 3251 D is almost amorphous. When FCP is introduced, X_c is more than doubled. The modified Ingeo 3260 HP shows a higher value even in the absence of the nucleating fibers. Again, the addition of FCP leads to an increase, but to a minor degree compared to D. Only when increasing tool temperature to 120°C, thus allowing for crystallization in the mold, X_c values above 50 % can be achieved. Surprisingly, despite having a nucleating effect, FCP seems to decrease crystallinity under these conditions. Lee et al. and Mathew et al. have published similar results for PLA reinforced with bamboo and lignocellulosic fibers, respectively [5;10]. Most likely, after having nucleated crystallization, the fibers also inhibit the further growth of impinging spherulites later in the process, thus reducing overall X_c values.

3.2 Mechanical Properties

In the following, the mechanical properties of the PLA composites are discussed as functions of the FCP content and the tool temperature.

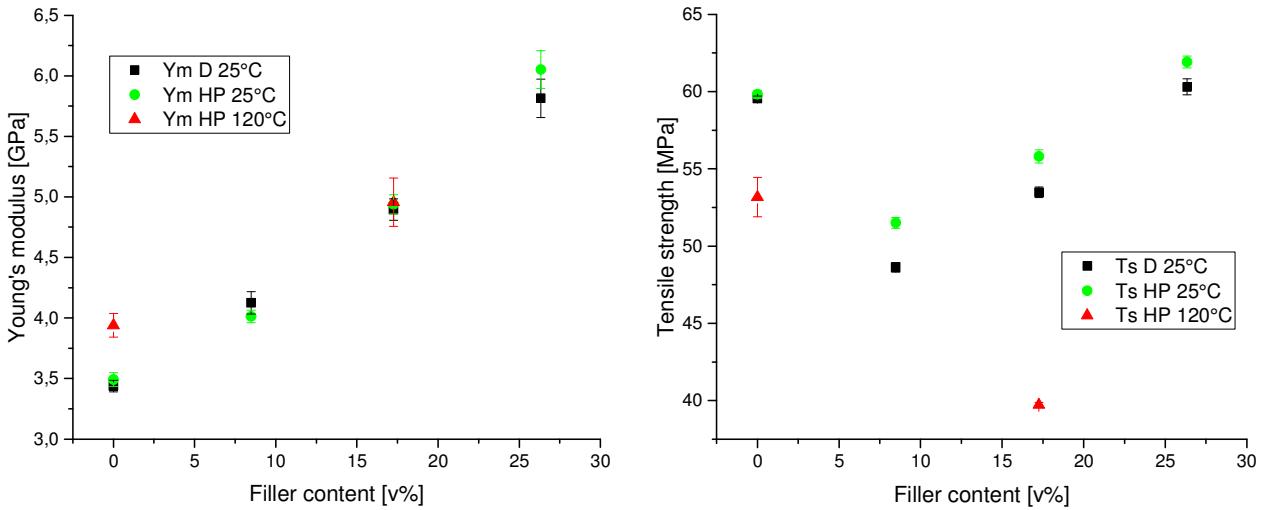


Figure 4: Young's modulus (Y_m ; left) and tensile strength (T_s ; right) of PLA and its composites as a function of FCP content in [v%] and IM tool temperature.

As Figure 4 shows, the tensile properties of the PLA composites tested are influenced by fiber content and tool temperature. Young's modulus basically increases linearly with fiber content (Figure 4, left). The effect of tool temperature, and thus crystallinity, is significant for neat PLA. As expected, an increase leads to a higher Y_m value. For the reinforced PLA, this is not observed. This can be explained by the FCP having a slightly negative effect on the X_c value under these conditions, as shown in Table 5. Furthermore, the pronounced reinforcement by the fibers probably masks the influence of morphology.

Obviously, the effects on tensile strength are quite different (Figure 4, right). For specimens produced with a tool temperature of 25°C, T_s decreases with the addition of FCP, and then increases again linearly with fiber content. Probably, because of a lack of a coupling agent for PLA, defects introduced by the fibers reduce tensile strength. The reinforcing effect of the FCP begins to dominate only at around 20 v% fiber content. It can only be speculated why Ingeo 3260 HP delivers slightly higher T_s values in the composites. Maybe, the lubricant included improves wetting of the fiber surfaces by the polymer melt and thus improves stress transfer in the solid state. It is quite surprising that the specimens produced at the higher tool temperature provide significantly lower T_s values. In the scientific literature, strength is normally reported to increase when increasing PLA X_c by lubricants and/or elevated tool temperature [11;12]. Probably, the very long injection molding cycle time (Figure 1) had caused polymer degradation [8] in our case. Despite having experienced a significantly lower thermic stress in injection molding, the tensile strength of the composite is even lower compared to the neat PLA. Maybe, defects introduced by the fibers have a more pronounced effect at higher X_c values, or interfacial adhesion is reduced in that state. However, these interpretations remain speculation as yet.

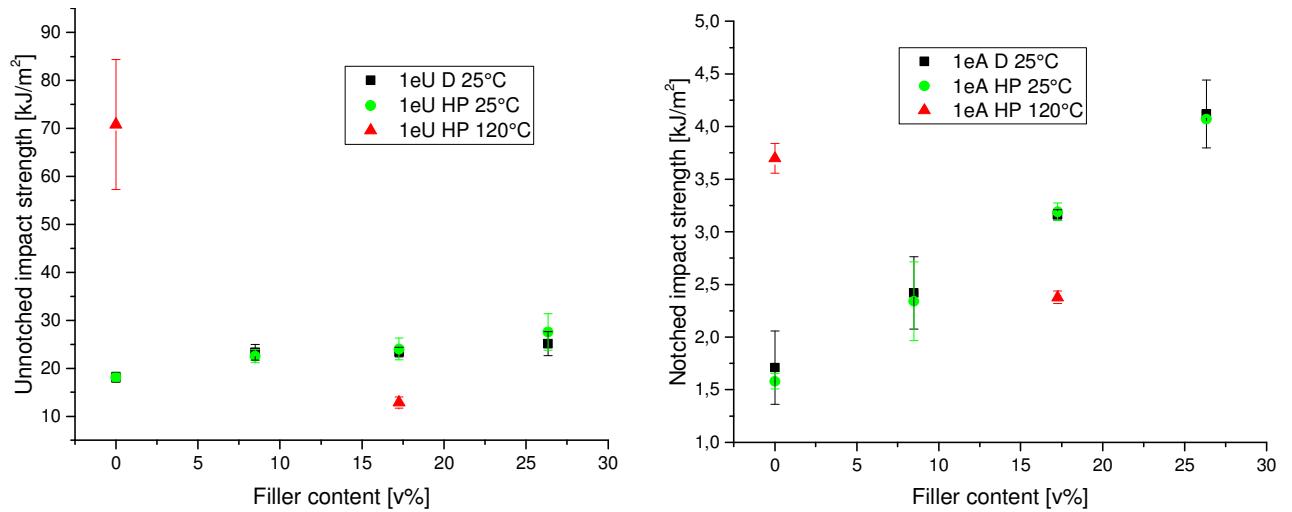


Figure 5: Unnotched (1eU; left) and notched Charpy impact strength (1eA; right) of PLA and its composites as a function of FCP content in [v%] and IM tool temperature.

Figure 5 shows that the impact performance of PLA can be influenced significantly by reinforcement and injection molding tool temperature, respectively. For unnotched specimens (Figure 5 left) injection molded with a tool temperature of 25°C, impact strength increases slightly with FCP content. This can be attributed to a significant contribution of fiber pullout to energy dissipation. For the higher tool temperature, quite different results are obtained. The impact strength of the neat PLA is increased by almost 4 times by increasing its X_c value via processing. Unfortunately, this is not the case for the respective composite, which performance is even decreased.

Quite similar trends are observed for notched impact strength. Here, for specimens produced with a tool temperature of 25°C, the increase in performance with fiber content is even more pronounced. This is because fiber pull-out particularly contributes to energy dissipation during crack propagation, which dominates in notched impact testing. For the higher tool temperature, basically the same trend is observed as for unnotched impact strength: The neat polymer shows an increase in performance of more than 100 %, while the respective composite experiences a decrease.

Based on mostly amorphous PLA, the effects of FCP reinforcement on impact performance confirm expectations based on the constituent properties. However, the influence of tool temperature, and, in turn, crystallinity (Table 5), is surprising. To our knowledge, a comparable increase in PLA impact strength resulting from a change in polymer morphology has not been reported in the literature before. Because this is so unexpected, we tested the reproducibility several times, and were able to confirm the result. As yet, we cannot explain the phenomenon thoroughly. Probably, intercrystalline tie molecules slow down crack propagation in crystalline PLA [13]. As to the unexpectedly low impact performance of the respective composite, this question remains open, as well. Investigations to clarify these issues are currently under way.

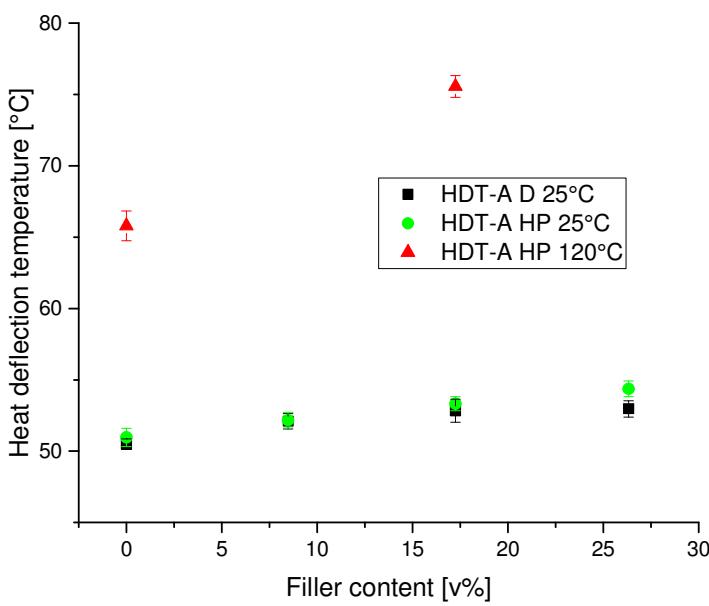


Figure 6: Heat deflection temperature (HDT-A) of PLA and its composites measured in mode A as a function of FCP content in [v%] and IM tool temperature.

Figure 6 shows that for specimens produced with a tool temperature of 25°C, reinforcement with FCP leads to a rather minimal increase in HDT-A. This is because as long as the polymer matrix is mostly amorphous, heat deflection temperature cannot exceed the glass transition temperature significantly. When increasing tool temperature from 25°C to 120°C, the X_c value of Ingeo 3260 HP is increased more than 3-fold, resulting in a 30 % increase in HDT-A. Based on this matrix with a X_c value of more than 50 %, introduction of 17 v% FCP leads to quite a significant further enhancement. Basically, these results are in line with those published in studies of comparable composite systems [4;12].

4 CONCLUSIONS

In this study, we have shown that man-made regenerated cellulose fibers Tencel® FCP can be used to significantly expand the property profile of PLA and thereby generate 100 % bio-composites. The fibers show a nucleating effect, allowing the lubricant-modified Ingeo 3260 HP to crystallize when cooled from the melt at 10 K/min, which does not happen in their absence. This results in a reduction in injection molding cycle time of up to 50 % at a tool temperature of 25°C, and of over 80 % for a tool temperature of 120°C (starting from an impractical value of over 470 s).

Table 6: Effects (in [%]) of the reinforcement of PLA Ingeo 3260 HP with 20 wt% of FCP on its mechanical properties.

Tool temp. [°C]	Ym	Ts	1eU	1eA	HDT-A
25	+41	-7	+33	+102	+5
120	+26	-25	-82	-36	+15

Based on PLA with a X_c value below 25 %, as obtained at the lower tool temperature, Young's modulus (Ym), and unnotched (1eU) and notched impact strength (1eA), respectively, can be increased significantly by reinforcement with 20 wt% of FCP. Based on PLA with a X_c value of above 50 %, as obtained at the higher tool temperature, only Ym and

heat deflection temperature (HDT-A) can be improved, while 1eU and 1eA decrease (Table 6). The latter is mostly because of the dramatic rise in impact performance of neat PLA upon the respective increase in crystallinity. To our knowledge, the latter phenomenon has not been reported before. An investigation of the underlying mechanisms is currently ongoing.

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