Advanced fibre reinforced thermoplastic composites with reduced processing times by use of nanoscale fillers

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Abstract. The industrial standard for the manufacturing of fibre reinforced thermoplastic composites (FRTCs) is the film stacking method. An alternative to this is commingling thermoplastic fibres with reinforcing fibres into hybrid rovings. These rovings are woven into weaves and consolidated through compression moulding. This paper evaluates the effects of 5 weight percent (wt.-%) titanium dioxide (TiO₂) in commingled polyamide 6 (PA6) on the cycle time during the consolidation process and the mechanical properties. A product representing the industrial standard is used as reference. In order to achieve a good comparability with this product, the film stacking process is also reproduced. Finally, the three plate types are compared regarding their consolidation, tensile and flexural strength. The results show that the hybrid roving FRTC is more consolidated, has better mechanical properties and enables shorter cycle times when compared to the film stacking process.

1. Introduction
The importance of light weight construction in the mobility sector has increased throughout the recent years. Both the automotive industry and the aerospace industry aim to achieve the lowest possible weight, whilst maximizing mechanical properties [1]. A reduced weight leads to higher energy efficiency, thus decreasing operating costs. In order to achieve this goal, fibre reinforced thermoplastic composites (FRTCs) are being developed [2]. FRTCs are made out of two or more components. The reinforcing fibres define the mechanical properties of the composite. Commonly used fibres are carbon, glass, aramid or basalt fibres. The matrix component defines the thermal properties, as well as enables a force distribution between the reinforcing fibres. Typical thermoplastic matrix components are polyamide 6 (PA6), polypropylene (PP) and polyether ether ketone (PEEK). FRTCs can be produced using the film stacking method. This involves stacking the two components into a sandwich structure and consolidating them through compression moulding. Alternatively, FRTCs can be produced by commingling thermoplastic fibres with reinforcement fibres into hybrid yarns or rovings and weaving these into fabrics. The textile structures are subsequently heated and consolidated through compression moulding. For an optimal consolidation, the temperature distribution needs to be homogenous throughout the composite, as excessive temperatures can lead to degradation of the polymer and low temperatures lead to consolidation constraints. The heating and cooling times are an essential component to this process, but are also the cycle time determining factors to the production chain. Shorter cycle times lead to higher outputs, thus reducing the costs per part. Thus the goal is to find the shortest cycle time, without compromising the consolidation quality. During the course of the “NanoOrgano” project for the Federal Ministry of Education and Research (BMBF) of the German
government, nanoscale titanium dioxide (TiO\textsubscript{2}) fillers were added to the thermoplastic component and a shortening effect on the heating and cooling times of the hybrid yarn based thermoplastic composites was observed [3]. The production chain suggested by this study is shown in Figure 1. The goal of the follow-up project “VIP Organo” is the validation of the innovation potential of this effect. As a first step in the project, studies looking into Polyamide 6 (PA6) compounds containing different concentrations of TiO\textsubscript{2} are being conducted.

![Figure 1. Production chain of the BMBF project NanoOrgano [3]](image)

The modification of PA6 with nanoparticles of TiO\textsubscript{2} has several effects. A small increase in the concentration of titanium dioxide (TiO\textsubscript{2}) leads to an increase in the thermal conductivity and a decrease in the heat capacity [4]. This leads to shorter heating and cooling times, which in turn have a significant effect on the cycle time during the consolidation process. In addition, the particle orientation is decreased, which reduces the characteristic thermal shrinking of the thermoplastic compound, and thus enables an easier thermal processing of the material. However, the concentration cannot be increased indefinitely as the TiO\textsubscript{2} particles also lower the strength of the compound [3]. Therefore, a compromise needs to be made. The results of Brüll et al. [4] show that the most promising concentration of TiO\textsubscript{2} is 5 wt.-%. This study therefore focused on the influence of the 5 wt.-% of TiO\textsubscript{2} in commingled PA6 on the mechanical properties, the consolidation and the cycle time during the production of FRTCs.

2. Methods
In order to assess the effect on the cycle time and compare it with the industrial standard this study compares three different FRTCs. The first one is an industrially produced FRTC. This composite is used as a reference and thereby defines the benchmark regarding the material properties of the other two. The second is produced using the commingling method. This composite has the same material properties as the first. However, the PA6 used has been modified with 5 wt.-% of TiO\textsubscript{2}. Since the production parameters of the industrially produced FRTC are unknown, a third composite needs to be manufactured. This is done by replicating the production process (film stacking) of the industrially produced FRTC while using the production parameters of the hybrid roving FRTC discovered during pre-tests. This enables a direct comparison between the second (film stacking) and third (hybrid roving) composites and thus makes deductions in regards to the first (industrially produced) composite possible.
2.1. Industrially produced FRTC
The Tepex® Dynalite 102-RG600(10)/47% black Typ B (Tepex) of the Bond-Laminates GmbH, Brilon, Germany is produced using the film stacking method and is chosen to represent the industrial standard. This composite, due to its good mechanical properties, and its production method is widely used by the automotive industry. The material properties are as follows: the glass roving weave is a 2/2 twill weave with a glass roving fineness of 1200 tex. The PA 6 matrix material is added as films. The resulting FRTC has a fibre weight percentage of 63 % and a plate thickness of 5 mm [5][6].

2.2. Hybrid roving FRTC
For the production of the hybrid roving FRTC, a glass roving with a fineness of 1200 tex is used. The PA6 utilised is the nano-modified PA6 with 5 wt.-% TiO2, which is spun into a roving with a fineness of 800 tex. These components are mixed into a hybrid roving with a fineness of 2000 tex using the commingling method. This method involves feeding the separate rovings into an air jet. In order to process these rough materials, with a combined fineness of 2000 tex, a customized air jet is used. During the commingling process the pressurised air and the resulting turbulences open the two different rovings to their filaments and then entangle them. Ideally, the manufactured hybrid roving has an even distribution of the thermoplastic filaments between the glass filaments. This reduces the distance the PA6 needs to flow during the consolidation process. In order to achieve good properties, pre-tests are conducted. The best parameters are then chosen for the production of the hybrid roving which is afterwards woven into a 2/2 twill weave and consolidated using a heating press.

2.3. Film Stacking FRTC
This composite is produced using the production method (film stacking) of the Tepex plate, while using the process parameters of the hybrid roving process. Therefore, a glass roving 2/2 twill weave and a PA6 films are used. The components are stacked in a sandwich structure in accordance with the reference materials specifications. This enables the production of plates equal in thickness and fibre mass ratio to the Tepex plate. The resulting stacks are consolidated in a heating press. This enables a direct comparison between the two production types and allows inferences to be made regarding the industrial process.

2.4. Consolidation & Analysis
During the consolidation process the material stacks are placed into the heating press at the consolidation temperature (Tc) of 250 °C. This is done in order to eliminate the effect of the heating up stage of the press tools on the consolidation process. At this temperature the pressure in the cavity (p) is maintained at 18 bar for different holding times (th) (0 s, 30 s, 60 s). Afterwards the tools are cooled to the extraction temperature (Te) of 180 °C and the consolidated plate is removed. In the second part of the experiment the effects of cavity pressure are investigated. In order to do this, the holding time (th) is kept at 30 s, while the pressure (p) in the cavity is changed (10 bar, 14 bar, 18 bar). These parameter combinations are used in the production of both the hybrid roving FRTC and the film stacking FRTC. The resulting plates for each parameter combination, as well as the Tepex plate, are then compared regarding their consolidation and mechanical properties. In order to evaluate the consolidation of the three different plates, two different analysis methods are used. Firstly, an examination under a light microscope is undertaken. During this process the probes are placed in epoxy resin. The epoxy resin fixates the different components during probe preparation (polishing) and enables equal probe quality in a test series. Afterwards the probes are analysed under the light microscope and the visible consolidation is evaluated. The second method is the micro computed tomography (micro-CT) scan. This method involves scanning a whole FRTC plate with x-rays. This method enables an inspection of the exterior surface, as well as the interior of the complete FRTC.

The mechanical properties are investigated using tensile and flexural tests. This is done in order to determine the parameter combination that enables a short cycle time, while maintaining high mechanical properties of the composite.
3. Results
A suitable commingling process is determined by pre-tests. The resulting hybrid rovings are analysed regarding the maximum force \(F_{\text{max}}\) that can be applied in accordance with the DIN EN ISO 2062 norm. The distribution is evaluated using light microscopy. It is observed that the maximum force which can be applied to the hybrid roving is overall lower than that of the pure glass roving. At the same time a negative correlation between the distribution of the filaments and the maximum force can be detected. The better the distribution becomes, the lower the maximum force appears to be. This enables a choice of commingling parameters for the production of the hybrid roving for the main experiments. For the further tests an average hybrid roving, with medium tensile strength and distribution, is chosen. The consolidated hybrid rovings, together with the film stacking and Tepex plates, are separately investigated in regards to their consolidation, tensile and flexural strength.

3.1. Light microscopic analysis
For each of the parameter combinations, a probe is prepared and viewed under the light microscope. The results show that during the consolidation process of the film stacking FRTC, the PA6 does not flow in-between all the glass filaments. Figure 2 shows the empty gaps as being filled with epoxy resin. Furthermore, distinct layers remain visible. This effect is observed throughout all the tested parameter combinations. However, an increase in the holding time \(t_h\), as well as an increase in pressure \(p\), is shown to improve the distribution.

The Tepex probe is shown to contain the same distinct layers as the film stacking FRTC probes (see Figure 2). However, an inspection of the area around the separate glass filaments shows that the PA6 flows in-between the filaments, while still not achieving an even distribution. The probes of the hybrid roving FRTCs, on the other hand, display a good distribution of the PA6 (see Figure 2). The filaments are well impregnated and there is no distinct layer of PA6 visible between the glass roving weaves. An increase in holding time \(t_h\) and a decrease in pressure \(p\) improve the distribution.

3.2. Micro-CT analysis
A micro-CT scan enables a clearer evaluation of the consolidation throughout the composite. However, due to similar radiation absorption of the PA6 and glass rovings, a clear view of the consolidation and impregnation of the filaments is not possible. Figure 3 shows the resulting pictures of the different plate types.
Although these pictures do not enable an evaluation of the consolidation of the filaments, they do show the different weave structures in the FRTCs. The weaves of the film stacking and the Tepex probe are still clear and well structured. However, the image of the hybrid roving FRTC shows larger gaps and a less clear structure, indicating that the glass fibres are not perfectly aligned.

3.3. Tensile test

The tensile strength ($\sigma_M$) is examined in accordance with the DIN EN ISO 527-4 norm. The results can be seen in Figure 4.

It is shown that the tensile strength ($\sigma_M$) of the film stacking FRTC improves with an increasing holding time (th) and increasing cavity pressure (p). However, the hybrid roving FRTC displays similar strengths even with an increased holding time (th). Interestingly, the strength increases with decreasing cavity pressures (p). Overall the strength is higher than that of the film stacking FRTC with
an exception at the sample produced with 18 bar pressure and 60s holding time. The industrially produced Tepex outperforms both plate types for all the parameter combinations.

3.4. Flexural test
The flexural strength ($\sigma_{FM}$) is examined in accordance with the DIN EN ISO 14125 norm. The results are shown in Figure 5.

![Figure 5. Results of the flexural tests](image)

The flexural strength behaves in a similar way to the tensile strength. It increases for the film stacking FRTC when the holding time and the pressure increase. For the hybrid roving FRTC, the holding time and pressure result in similar flexural strengths. The Tepex plate clearly achieves significantly higher strengths.

4. Discussion
The commingling pre-test illustrate a weaker maximum force can be applied to the hybrid roving in comparison to the pure glass roving. This may be explained with the structure of the hybrid roving. The glass filaments are no longer perfectly straight, but wound and entangled. This leads to an uneven force transmission between the separate filaments. Due to the entanglement with the PA6 filaments, it is to be expected that this effect can be reduced after consolidation. Nevertheless, a trend can be seen. The better the distribution of the different filaments is, the lower the maximum force appears to be. This means a compromise between strength and distribution needs to be made.

A comparison of the consolidation of the different plate types, for all the parameter combinations, shows a clear trend. Even though the consolidation of the film stacking FRTC increases with an increased holding time and pressure, it cannot compete with the consolidation of the hybrid roving FRTC. Not even the industrially produced Tepex plate achieves a comparable distribution of the PA6 between the glass filaments. This may be due to a combination of the nano-modification and the hybrid roving structure produced by commingling the two components. The hybrid roving FRTC is shown to be well consolidated for all the parameter combinations, which suggests that they can be
produced with a lower cavity pressure, a lower holding time and thus reduce the cycle time and production costs. This may be due to the nano-modification, which increases the thermal conductivity and decreases the heat capacity. However, in order to clearly distinguish between the impact of the nano-modification and the commingling method, further experiments need to be conducted. It may be helpful to have a study looking into a nano-modified film stacking FRTC, a hybrid roving FRTC without a nano-modification, as well as an investigation into the minimum cavity pressure needed for consolidation.

When evaluating the results of the tensile test it needs to be taken into account that the probe length set by the norm cannot be met. The length is 200 mm instead of 250 mm. The clamping surface size is maintained, while the measuring length is adjusted. However, as the probe dimensions of all the different probe types are the same, a comparison can be made anyway. The results of the tensile tests show that the hybrid roving FRTCs are stronger than the film stacking FRTCs produced with the same parameter combination. This may be due to the better distribution of the PA6 between the glass filaments, which enables a better force transmission to the reinforcing glass roving filaments. This theory is supported by the CT-pictures. The scans show that the glass roving weaves of the Tepex and film stacking plates maintain their tight weave structure, while those of the hybrid roving plates do not. This is likely due to the commingling process during which the components are mixed. The resulting hybrid roving weave is made out of a roving containing both components. In the film stacking process the glass roving weave is added separately and therefore maintains its structure after consolidation. The only exception to these findings can be observed at the samples produced with 18 bar pressure and 60 s of holding time, where the film stacking FRTC show a higher tensile strength then the hybrid roving FRTC. The tensile strength of the film stacked FRTC rises due to a better impregnation of the fibres and surpasses the hybrid roving FRTC due to less fibre damage during production. However, the direct comparison of the two processes shows that the better consolidation of the hybrid roving FRTC outweighs the benefits of a tighter and more aligned structure of the reinforcing glass roving weave achievable using the film stacking method. Interestingly, the strength of the hybrid roving FRTC increases with decreasing cavity pressures. A possible explanation is that higher pressures result in a reduced porosity of the fabric, leading to an uneven distribution of PA6 and contributing to the loss in strength. Therefore, the effects of the cavity pressure on the strength should be further investigated. As the costs of production plants rise significantly with their pressure capacity, using lower pressures also has the potential of significantly lowering investment costs.

The results of the flexural tests show a similar trend to the tensile tests. The film stacking plates are more resilient with increasing pressure and holding time. The hybrid roving plates show a similar strength for different holding times and cavity pressures. However, the results of the flexural tests at 18 bar and 60 s, (see Figure 5) seem to show a decrease in strength. This might be due to increasing cavity pressure resulting in damage to the glass fibres or a long holding time causing the PA6 to decompose. However, as these results are not observed for the film stacking process or in the tensile tests, this is not consistent. The result for this parameter combination may be an anomaly and further studies should elucidate this and investigate possible causes.

In general, when evaluating the flexural test results, it has to be taken into account that the probes do not fracture according to the norm. All the probes, apart from the Tepex one, develope interlaminar fractures. This is reflected in the low flexural strength values displayed by the two self-made probe types. Due to this, a comparison between the two remains possible. This shows that the hybrid roving is stronger for the tested parameter combinations. The interlaminar fractures may result from an inadequate sizing on the glass fibres, as it probably differs between the tested glass fibres and the glass fibres used for the Tepex plate.

The Tepex plate proves to be the strongest in the tensile and flexural tests. As the production parameters are unknown, it is difficult to establish the source of these mechanical properties. However, it suggests that there is scope to adjust parameters further than this study investigates, to achieve a better result. The comparison between the two self-made plate types remains an important

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finding, as it shows that under the same conditions, nano-particles, combined with commingling, are superior to the traditional film stacking method.

5. Conclusion
From this study it can be surmised that the nano-modified hybrid roving FRTC enables shorter cycle times, while achieving good mechanical properties. The consolidation and impregnation of the glass filaments are clearly better, even in direct comparison with the industrial standard. The tensile and flexural tests highlight the possibility to achieve shorter cycle times, while maintaining high levels of strength. These properties allow a balance between keeping production costs down and maintaining the integral properties. However, further investigation needs to be conducted. In particular, the differentiation between the two overlapping effects of the nano-modification and the hybrid roving need to be examined. Nevertheless, both the process and the material demonstrate promising potential for the future of FRTCs.

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