IMPACT OF THE MANUFACTURING PROCESS OF LOCALLY LOAD-RELATED REINFORCED COMPOSITES ON THE INTERFACE BEHAVIOR

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Keywords: Hybrid structures, in-situ tape placement, interface behavior, crystallinity

1 General Introduction
Due to the raised environmental awareness of the society and legal requirements concerning national emission ceilings the main focus of the automotive industry is the substitution of conventional materials like steel through weight optimized structures like fiber reinforced polymers. The high requirements and the need of continuously improved materials cannot be fulfilled only by the synthesis of new polymers or matrix-homogeneous composites. An alternative to that issue is the mixture of two or more composite material partners based on polymers with the aim to increase the mechanical properties combined with an overall weight reduction. The main element of this study is the build-up of hybrid structures by combining two different lightweight production methods in order to locally reinforce a semi-finished part. On the one hand the latter is produced by stamp forming process of a bidirectional endless fiber reinforced PP-GF sheet material, on the other hand the local unidirectional endless tape reinforcements are applied by use of thermoplastic in-situ tape laying process (TTL) [1].

Based on the interest of the automotive industry to produce cars with lightweight properties and to integrate PP-GF organic sheets (OS), type TEPEX dynalite® 104-RG600(4) (PP), with a fiber volume content of 47 %, supplied from Bond Laminates, are used as base material for this study. Unidirectional tapes from Ticona type CELSTRAN CFR-TP PP-GF, with a width of 12 mm, are used as local reinforcements (Tab 1).

The specimens build of organic sheet plus tapes are produced on the one hand by use of a 7 axis robotic thermoplastic tape placement system (Fig. 1). As a heat source a hot gas torch with a mixture of H₂, O₂ and air is used to heat up the incoming tapes and the substrate. On the other hand in order to produce reference specimens an autoclave is used.

2 Objectives
The critical element concerning the mechanical properties of the realized hybrid structure is the interface zone between tape and organic sheet which needs detailed investigation. For optimizing this interface and the quality of the resulting hybrid structures based on the combination of stamp forming and thermoplastic in-situ tape placement process, the parameters tape placement velocity (v₀) as well as hot gas volume flow (v) are determined in an analytical and experimental way.

The specimens are examined among others by Double-Cantilever Beam (DCB) test according to ASTM D 5258 in order to determine the energy release rate G_{ik}, which is an indicator for the quality of the bonding behavior. In addition the results are compared to samples that are produced using the autoclave which offers optimal conditions for the time-dependent polymer diffusion at the interface. Detailed investigations of the molecular phenomena that take place within the contact zone are performed by microscopic cross sectional analyses as well as 3D computed micro-tomography. Differential Scanning Calorimetry and Thermogravimetric analysis (TGA) are processed to determine the relationship between crystallinity and the energy release rate. Furthermore, microindentation hardness tests were performed.

3 Results and Discussion
It is known that an optimal configuration of process parameters has a linear dependency between tape placement velocity and thermal input, i.e. hot gas volume flow.[2]

In order to determine the optimal process parameters for the tape placement process the interface behavior between tape and organic sheet is examined by performing Double-Cantilever Beam tests according
to ASTM D5528. Usually, DCB tests are used to determine the resistance of a material against interlaminar crack propagation [3] which for example may occur in the interface between two materials. In [4] symmetric specimens are required which means that the separating foil shall be arranged in the center plane of the laminate between organic sheet and tape. For an organic sheet with a thickness of 2 mm there are 8 tape plies required for a symmetric system. Since the Young’s modulus $E_1$ of the tape is much higher than the modulus of the organic sheet, the tape is much more rigid and bend-proof. A symmetric build-up leads to bend and break of the organic sheet before the delamination starts (Fig. 2).

On this account specimens were produced with a symmetric system concerning the bending stiffness according to equation 1.

$$E_T I_T = E_{OS} I_{OS}$$  \hspace{1cm} (1)

$E_x$ is the Young’s modulus of tape (T) and organic sheet (OS), $I_x$ is the bending stiffness of T and OS, which can be calculated as

$$I_x = \frac{h_x^3 \cdot b}{12}$$  \hspace{1cm} (2)

where $h_x$ is the thickness of T and OS, and $b$ is the width of the specimen. The ideal amount of tape plies according to equation 1 is 6.5 layers, whereas to simplify the matters an amount of 6 tape plies is used for the DCB specimens.

For the investigation of the influence of the thermal energy on the quality of the in-situ tape placement process different production methods are used for the build-up of the hybrid structure which differ in the placement velocity. In addition, one hybrid structure is produced using the autoclave. The process parameters are summarized in Tab 2.

It can be observed that a combination of 6 Nl/min hot gas flow and 6 m/min velocity are the optimal process parameters. Specimens produced within this process window show an energy release rate that is twice as high as the energy release rate of specimens that are produced using the autoclave (Fig. 3).

This phenomenon occurs although the in-situ tape placement process is characterized by a very fast consolidation step which does not provide optimal conditions for polymer diffusion at the interface. A 1000x enlargement of the interface made in the scanning electron microscope shows plastic deformation of the PP in the interface which is also an indication for very good interface bonding between the hybrid partners (Fig. 4).

In order to predict interface properties depending on the process parameters of the in-situ tape placement process there is a need for a better understanding of the complex thermal processes.

For the calculation of the optimal conditions for the hot gas volume flow Differential Scanning Calorimetry (DSC) analyses are performed to determine the thermal capacity of tape and organic sheet (Fig. 5).

The thermal capacity curve is divided for the calculation into 1619 segments of approximately 0.15 °C in near-linear regions between two temperatures to obtain an average of the temperature-dependent heat capacity for each area. The optimal conditions for the hot gas volume flow are calculated by means of thermal output $\dot{Q}_T$ according to equation (3), where $\rho_T$ is the density, $v_T$ is the velocity, $w_T$ is the width, $t_T$ is the thickness, and $c_p$ is the isobaric thermal capacity of the tapes. \[2\]

$$\dot{Q}_t = \sum_{i=1}^{1619} \dot{Q}_i = \rho_T v_T w_T t_T \cdot \sum_{i=1}^{1619} c_p(T_{i+1} - T_i)$$  \hspace{1cm} (3)

Fig. 6 shows the calculated thermal output in dependency of tape placement velocity that is needed to heat up the tape at 275°C. It can be seen that a higher tape placement velocity requires a higher heat flow. The heat flow depends on the heat capacity of the hot gas torch, and the volume flow of the combustion gas, which is a hydrogen-oxygen mixture (ratio 9:1). In a first step the flame temperature $t_v$ is calculated according to equation (4), where $H_x$ are the respective exhaust gas enthalpies according to [5], assuming that the exhaust gas components will not dissociate under high temperature. The value of $t_v$ is 2511 °C.

$$t_v = t_{v1} + \frac{(h_{a1} + h_a + h_{a2} + h_2)}{h_a2 - h_{a1}} \cdot (t_{v2} - t_{v1})$$  \hspace{1cm} (4)

A method to determine the flame temperature taking into account the dissociation is the calculation of the exhaust gas enthalpy $h_a$ according to equation (5), where $\nu_{a,f}$ is the moist exhaust gas, which consists
of the water gas and N₂ from the atmosphere, combined with a graphical method for determination of the exhaust gas temperature in Fig. 7. [5]

\[ h_a = \frac{H_{u,n} + H_B + H_L}{v_{a,f}} \]  

(5)

Thereby, the specific temperature is independent from the hot gas flow and amounts to 2360 °C.

Considering the fact that a combination of 6 Nl/min hot gas flow and 6 m/min velocity leads to the best interface results, it can be assumed that the tape with the usage of these process parameters is actually heated up to an ideal temperature where the matrix is in the molten state, but the degradation \((T_{\text{deg}} \approx 300 \, ^\circ C\) \([6]\)) does not start. For PP this temperature is approx. 275 °C. With regard to the thermal output it can be calculated that only 1.81 % of the thermal power reaches the tape. On this basis, a realistic prediction of the correlation between velocity, gas flow, and interface quality can be made and summarized in a 3D chart. In Fig. 8 these optimal process configurations are presented in accordance to \(G_{\text{ic}}\).

The very high energy release rate, which is representative for a very good interface behavior of the specimens produced using the in-situ tape placement process, is directly influenced by 3 phenomena.

3.1 Influence on the zone of plastic deformation through fiber migration in the interface

Within the autoclave process all matrix material is in molten state, which allows an optimal condition for the interaction between the polymer chains and thus, polymer diffusion. Due to the fact that all matrix material is in molten state, the reinforcing fibers are able to diffuse in the interface, too. An explicit and well-defined polymer interface without fibers is not recognizable compared to the specimens that are processed by in-situ tape placement process (TTL) as shown in microscopic cross sectional analysis (Fig. 9 and Fig. 10).

The before mentioned was approved by use of 3D computed micro-tomography system (brand: Phoenix x-ray systems + services GmbH) and visualized with Volume Graphics Studio Max. Regarding the sample produced by use of TTL a characteristic, well-defined polypropylene interface zone between the organic sheet and the tapes could be detected through the entire specimen (Fig. 11, yellow: polymer interface zone).

In contrast the specimen processed in the autoclave shows no well-defined polymer interface zone between OS and tape. (Fig. 12)

The interface that consists of pure polymer (PP) in the case of the tape placement process offers a much more ductile behavior, compared to the interface that is interspersed with fibers. In the case of fracture-mechanical analysis (DCB, mode I) the fibers affect the fracture propagation in the contact zone (Fig. 13), consequently the specimens produced in the autoclave show a brittle crack characteristic behavior and are therefore characterized by a lower value of \(G_{\text{ic}}\) \([3]\).

3.2 Crystallite structure

With respect to the before-mentioned conditions the two production methods offer totally different conditions for the formation of the crystallite structure. In order to determine the degree of crystallinity in a first step a thermogravimetric analysis were performed with the specimens produced in the autoclave and by TTL as well as the raw materials on a Mettler-Toledo TGA. Tab 3 shows the results of the TGA concerning the matrix net weight that is needed for further processing.

In a further step the melting enthalpy was determined by Differential Scanning Calorimetry analysis (Fig. 14) with a DSC from Mettler-Toledo. As heating and cooling rate 10 K/min was chosen.

The relative melting enthalpy \((H_f)\) of the raw materials as well as the relative melting enthalpy from the specimens produced either by autoclave or TTL were calculated and have values as shown below:

\[ \Delta H_{f,Tape} = 106.21 \, \text{J/g} \]
\[ \Delta H_{f,\text{Organic sheet}} = 85.07 \, \text{J/g} \]
\[ \Delta H_{f,\text{Autoclave}} = 96.77 \, \text{J/g} \]
\[ \Delta H_{f,TTL} = 88.41 \, \text{J/g} \]
The degree of crystallinity ($\alpha$) was calculated according to equation 6, where $\Delta H_{f100\%}$ is the melting enthalpy of a full-crystalline polypropylene given by the literature ($\Delta H_{f100\%} = 209$ kgkJ).[7]

$$\alpha = \frac{\Delta H_f}{\Delta H_{f100\%}}$$  \hspace{1cm} (6)

It could be shown that the polymer of the specimens processed in the autoclave offers a higher value of crystallinity compared to the specimens produced with in-situ tape placement process:

$$\alpha_{\text{Autoclave}} = 46.3 \%$$
$$\alpha_{\text{TTL}} = 42.3 \%$$

This can be explained due to the fact that the matrix is comparably long time in molten state while processing in the autoclave. While processing by thermoplastic in-situ tape placement process the material partners are only melted in the nip-point at the contact zone in a locally - both temporally and regionally - restricted area and are consolidated instantly after passing over. Through the limited time the crystallites cannot grow in a sufficient way and the interface zone is more ductile and characterized by a higher value of $G_{\text{IC}}$.

The ductility of the specimens at the interface is approved by microhardness testing (brand: Shimadzu). The specimens are consequently loaded up to 50 mN and the depth of indentation is measured. Thus, the dynamic hardness (Martens hardness) can be calculated. As indenter a Vickers diamond is used. The before mentioned can be seen as confirmed although the sampled data show large standard deviation: the specimens produced by TTL show a more ductile behavior (Fig. 15).

3.3 Molecular stretching and relaxation

If two polymers are in their molten state and they are brought together into intimate contact, which leads to an absorption of the macromolecules, a diffusion of the macromolecules through the interface of the two polymers emerges. The resulting adhesive strength is determined by various aspects and the total adhesive strength $\sigma$ is the sum of the contact adhesive strength $\sigma_{\text{contact}}$, the diffusion adhesive strength $\sigma_{\text{diffusion}}$, and the deformation/relaxation adhesive strength $\sigma_{\text{def/relax}}$ (equation 7) [9].

$$\sigma = \sigma_{\text{contact}} + \sigma_{\text{diffusion}} + \sigma_{\text{def/relax}}$$ \hspace{1cm} (7)

Since thermoplastic polymers do not possess inherent tack, the contact adhesive strength can be neglected in this case.

The diffusion adhesive strength is a time dependent process, which can be mathematically described as follows in equation 8

$$\sigma_{\text{diffusion}} = \sigma_{\infty} \left(1 - \frac{t}{t_r}\right)^{\frac{1}{n}}$$ \hspace{1cm} (8)

whereas $t$ is the diffusion time, $t_r$ is the time after the molecule completely escaped through the interface, the so-called reptation time, and $\sigma_{\infty}$ is the strength of the interface after an infinitely long period, that is the basic material strength (in this case PP) [9]. The interdiffusion of the polymer chains at the interface can be depicted as in Fig. 16. [9], [10] For clarity only one side of the interface is shown.

At the time $t_0$ the polymers are brought into intimate contact. The randomly oriented end segments of the polymer chains which are shown as points are beginning to escape from their old position. At the time $t_1$ a larger part of the chain escapes from its position and is able to diffuse through the interface, whereas $x$ describes the average penetration distance of the polymer chains at one side of the interface. After a longer period of time ($t_2$) the penetration distance and hence the interface thickness becomes larger. The maximum obtainable interface thickness is $2x_{\infty}$ and can be reached at $t = t_r$.

Since the contact time of the most joining processes is not long enough in order to achieve a sufficient reptation time $t_r$ and actually, the contact time during the tape placement process is very short, the adhesive strength is also determined by another effect, the so-called deformation and relaxation of the polymer chains. During joining the long polypropylene molecules at the interface are stretched due to the elongational flow of the PP melt. Afterwards, the chains relax and a process of polymer chain entanglement appears at the interface (Fig. 17). [9]

This effect is much faster than the diffusion of the polymer chains, whereas the relaxation time of the
chains $\tau_R$ is determined by the viscosity $\eta$ and the creep compliance $J$ of the polymer melt (equation 9).

$$\tau_R = \eta \cdot J \quad (9)$$

It is assumed that during the in-situ tape placement process the bonding strength between the material partners is not mainly caused by polymer diffusion at the interface, but due to very fast molecule stretching and relaxation phenomena. The contact zone that results from the in-situ tape placement process can be attributed to deformation/relaxation bonding strength, because the molecules are stretched by the pressure of the consolidation role in one direction and are relaxed during cooling. This leads to an entanglement of the molecular polymer chains. In contrast, a component manufactured in the autoclave can be attributed to diffusion bonding strength. The molecules are not stretched in this case, but the bonding behavior can be assigned to autohesion and adhesion phenomena [11].

4 Conclusion

The influence of the production method for application of local reinforcements on polymer based thermoplastic organic sheets by in-situ tape placement process compared to the autoclave process was examined. Optimal process parameters concerning the hot gas volume flow and the placement velocity for TTL process were determined in an analytical way. Direct influence of the process parameters as well as of the production method on the interface behaviour and thus, on the energy release rate $G_I$ of the two material partners could be determined.

It has been shown that the TTL process is suitable for the build-up of locally reinforced structures with a well defined polypropylene interface zone between the two material partners. Despite the very short processing time the mechanical behaviour of the interface (fracture propagation), which can be quantified by DCB mode I ($G_I$ value), is much better than the interface of the specimens processed in the autoclave, although this process offers optimal conditions for molecular interfacial diffusion. The reasons were discussed within this work.

It has been shown that on the one hand these phenomena correlate directly with the crystallization rate of the specimens, which is also influenced by the production method. On the other hand the TTL process offers a much more ductile behavior at the interface due to the non-presence of fibers in the interface zone. Furthermore, the adhesive strength of the interface partners is caused by molecular stretching and relaxation phenomena at the PP/PP interface, which provides a higher $G_K$ value than the time dependent diffusion process which occurs in the autoclave process.

References

Tab 1 Material properties

<table>
<thead>
<tr>
<th>Organic sheet</th>
<th>TEPEX dynalite 104-RG600 (4) (OS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibers</td>
<td>roving glass</td>
</tr>
<tr>
<td>Fabric</td>
<td>twill 2/2</td>
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<tr>
<td>Area weight</td>
<td>g/m²</td>
</tr>
<tr>
<td>Yarn</td>
<td>tex</td>
</tr>
<tr>
<td>Weight rate</td>
<td>%</td>
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<tr>
<td>Polymer</td>
<td>PP</td>
</tr>
<tr>
<td>Density</td>
<td>g/cm³</td>
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<tr>
<td>Fiber content</td>
<td>% vol.</td>
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<tr>
<td>Thickness per layer</td>
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<tr>
<td>Tensile strength</td>
<td>MPa</td>
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<tr>
<td>Ultimate stress</td>
<td>MPa</td>
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<table>
<thead>
<tr>
<th>Tape</th>
<th>CELSTRAN CFR-TP PP-GF70 (T)</th>
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<tbody>
<tr>
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<td>unidirectional glass</td>
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<td>Fiber content</td>
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<td>Matrix</td>
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<td>Width</td>
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<tr>
<td>Thickness</td>
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Tab 2 Process parameters

<table>
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<tr>
<th>Tape-placement</th>
<th>PP_GF_646</th>
<th>PP_GF_666</th>
<th>PP_GF_686</th>
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<tr>
<td>Hotgas-volumeflow</td>
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<td>6 [Nl/min]</td>
<td>6 [Nl/min]</td>
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<tr>
<td>Placement velocity</td>
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<td>6 [m/min]</td>
<td>8 [m/min]</td>
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<tr>
<td>Consolidation pressure</td>
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<td>4.5 [bar]</td>
<td>4.5 [bar]</td>
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<tr>
<td>Compaction roller temperature</td>
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<td>40 [°C]</td>
<td>40 [°C]</td>
</tr>
<tr>
<td>Autoclave</td>
<td>Temperature</td>
<td>Pressure</td>
<td>Time</td>
</tr>
<tr>
<td>PP_GF_AK6</td>
<td>190 [°C]</td>
<td>24 [bar]</td>
<td>20 [min]</td>
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Tab 3 TGA results

<table>
<thead>
<tr>
<th>Autoclave</th>
<th>TTL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start: 33.19 C</td>
<td>Start: 32.18 C</td>
</tr>
<tr>
<td>Weight Loss: -3.368 mg</td>
<td>Weight Loss: -4.448 mg</td>
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<tr>
<td>-19.509 %</td>
<td>-32.148 %</td>
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<table>
<thead>
<tr>
<th>Tape</th>
<th>Organic sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start: 44.50 C</td>
<td>Start: 32.77 C</td>
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<tr>
<td>Weight Loss: -1.011 mg</td>
<td>Weight Loss: -2.249 mg</td>
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<td>-23.093 %</td>
<td>-24.791 %</td>
</tr>
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Fig. 3 Energy release rates

Fig. 4 1000x magnification of OS interface

Fig. 5 Thermal capacity of tape and organic sheet

Fig. 6 Calculated thermal output in dependency of tape placement velocity

Fig. 7 $h_a$–$t$–diagram for calculation of flame temperature

Fig. 8 Optimal process parameters
Fig. 9 Microscopic cross sectional view of specimen produced with TTL

Fig. 10 Microscopic cross sectional view of specimen produced with autoclave

Fig. 11 3D Computed micro tomographical view of locally reinforced specimen (TTL)

Fig. 12 3D Computed micro tomographical view of locally reinforced specimen (autoclave)

Fig. 13 Impact on the plastic zone at the crack tip

Fig. 14 Differential Scanning Calorimetry analysis
Fig. 15 Martens hardness

Fig. 16 Diffusion process at the interface [10]

Fig. 17 Molecular stretching and relaxation at a PP/PP interface