Abstract

In this paper the results of a series of trials are discussed, where prepreg test panels are processed in an autoclave under different cure cycles while their cure progress is monitored by ultrasound sensors. The in-house developed sensors were applied to the mould at four different locations and used to monitor the cure progress throughout the complete autoclave process. The produced panels were inspected visually and by ultrasound scan and then tested for glass transition temperature and by three-point flexural tests. The manufacturer’s recommended cure cycle is used as reference for the process variations and the results of cure monitoring and thermal and mechanical tests for designing optimized processes.

The main goals of these investigations are the determination of the time saving potential of sensor guided processes and validation that similar mechanical properties are achieved.

The Need for Sensor Guided Cure Processes

The curing of the thermoset matrix by applying temperature and pressure is one of the most important production steps in manufacturing of carbon fiber reinforced plastic (CFRP) structures. The cure process significantly influences the final part quality and properties. Typically predefined temperature profiles are used consisting of one or more temperature dwell steps. The temperature profile is usually derived from the resin’s data sheet and then often adapted to the specific part design by trials. In order to ensure sufficient cure and to cope with unpredictable deviations, the dwell times are usually prolonged by high safety margins. Often occurring process deviations are inhomogeneous temperature distribution, variations in resin reactivity due to resin age or mixture and its temperature history. Due to the fact that their influence on the cure progress is not monitored during the running process, deviations cannot be corrected by adapting the process. This means that the process temperature profile has to be designed to assure sufficient cure under all circumstances and has to take deviations into account, which results in long cure cycles with high safety margins. In return this leads to long occupation times of the tools and machineries and hence to increased costs and low output.

For more efficient processes the cure progress itself has to be taken into account instead of using a fixed temperature profile. To achieve a process control as function of the cure progress, sensors are required, which are able to acquire the cure state during the running autoclave process. By monitoring the cure progress the information can then be used to terminate the dwell steps when the resin reaches sufficient cure. In many cases the temperature profile consists of two dwell steps, the first at a relatively low temperature and the second at final cure temperature. In the first step the resin is brought to gelation at a slow reaction rate to reduce residual stress and in the second step to complete cure.

Cure Monitoring System

There are numerous cure monitoring methods available such as dielectrical analysis, electrical resistance, ultrasound, infrared or Raman spectroscopy. Nonetheless, their application into the environment of industrial composite production is challenging or very limited. Dielectric sensors are already used in the aeronautic industry [1] as there are several commercial systems of high degree of maturity. The use of dielectric sensors exhibits the drawback that the sensors need to be in direct contact to the resin, but also need to be isolated from carbon fibers to prevent short circuit. These requirements need to be fulfilled although the degree of cure is obtained on the part’s surface. [2,3] Ultrasound sensors on the other hand have multiple advantages as they do not need any direct contact to the part itself, therefore the sensors are easy to integrate into the tool and do not affect neither the vacuum tightness nor the part surface. As another advantage ultrasound sensors obtain not only the
cure state on the part surface but a mean value through the part thickness. The most robust ultrasound technique for this application is the transmission method, where one sensor is used as transmitter generating sound impulses, which propagate through the part and another sensor on the opposite side of the part is acting as receiver. The cure progress is then determined by velocity of sound, which is linked to the degree of cure. [4–10] In state of the art technology, ultrasound cure monitoring is only applied to closed mould processes. Its adaption to open mould processes with a flexible vacuum membrane by special adaptors can be seen in Fig. 1. There are two possible variations, the first is to seal the adapter and the sensor into the vacuum bag and in the second they are placed on the vacuum bag and then held by another auxiliary vacuum bag.

Trials with the state of the art ultrasound transducers for cure monitoring showed unreliable measurements which could be linked to unstable acoustic coupling [11]. Usually the transducers are coupled by thin copper or lead foils to the mould and the adapters push them tightly against the mould surface [6]. Both are very sensible to temperature gradients, so that there is a high risk of losing acoustic contact where no sound waves can propagate between the transducers and the mould and hence the cure monitoring measurement is disrupted.

With a very simple idea the coupling can be prevented from failing. Instead of using an ultrasound transducer, where a piezoelectric element generates the sound waves which have to be propagated through the transducer’s housing and then coupled into the mould, piezoelectric ceramics were glued to the mould itself (Fig. 2), so that the mould becomes part of the sensor [12]. These sensors reach high signal strength, are small and hence easy to integrate, reliable and inexpensive.

![Fig. 1. Transducers in closed (left) and open (right) mould processes](image)

![Fig. 2. Piezoceramic ceramics glued to mould as ultrasound cure monitoring sensors](image)

The sensors are connected to an impulse generator for sending and a digital oscilloscope for signal reception and acquisition. The acquired signals are then analyzed for the time of flight and amplitude from which the ultrasound velocity and damping can be calculated.

4 Materials and Test Methods

The produced test panels consist of 16 unidirectional layers of the prepreg material MTM44-1 (UMECO Ltd.) with a thickness of approximately 2 mm and an area of 850 x 600 mm². The mould consisted of a steel plate and a thin steel cover plate, where each five piezoelectric ceramics were mounted. Due to limited cable interfaces in the autoclave only four sensor pairs could be connected at the same time. A layup, as represented by Fig. 3, was chosen to prevent resin bleeding and comparable laminate thicknesses throughout the test series. The borders of the prepreg and cover plate were framed by release film and only one thin glass roving per side allowed evacuation of the prepreg material, but almost no resin flow. The vacuum bag had a rectangular cutout and was sealed on top of the cover plate, so that the sensors remained accessible. The layup is derived from the application notes of the prepreg manufacturer [13].
To this point six different process cycles were performed, all derived from the prepreg data sheet and partially optimized based on sensor data (Fig. 4). The first process MTM 02 represents the standard cycle consisting of two temperature dwells of 2 hours at 130 and 180 °C. The profiles of MTM 03 and 04 are only composed of one dwell step at 180 °C of 2 and 4 hours duration as well as MTM 05 and 06 respectively at 130 °C with durations of 8 and 4.67 hours. The latter was obtained from analyzing the cure sensor data. The last process cycle MTM 07 was again the standard cycle with a prolonged first dwell step.

The panels are first trimmed and then scanned for voids or delaminations by ultrasound and then they are cut to coupons and tested for their mechanical properties by tension (0° and 90°), compression (0° and 90°), three point flexural (0°) and interlaminar shear tests. Furthermore, they are analyzed for remaining reaction enthalpy $\Delta H$ and glass transition temperature $T_g$. Unfortunately only the flexural tests and analysis of remaining reaction enthalpy and glass transition temperature have been performed to this point.

5 Results

5.1 Ultrasound cure monitoring

In the following the ultrasound cure monitoring results will be discussed in detail for one test panel and then the different processes will be analyzed and compared. During the test series many minor problems occurred in using this technique in autoclave environment and could be improved which resulted in higher measurement quality and robustness. Therefore the current last test is chosen for the detailed discussion of result. The process was also composed of two temperature dwell steps and hence demonstrates a typical process.

Fig. 5 compares the four time-of-flight plots obtained by the ultrasound sensors throughout the whole autoclave process. More precisely it does not show the absolute value but the shift of the time-of-flight, which was calculated by cross-correlating the signals to each other. The cross-correlation allows calculating offsets between the signals in a very high resolution and also robust signal analysis.

The plots represent the channels 1, 3, 5 and 7 where the ultrasound impulse was sent from the tool side and received from the sensors on the cover plate. On channels 2, 4, 6 and 8 the sound waves were sent in opposite direction which results in almost identical signals. The sensor positions are shown in the scheme in Fig. 5, where the arrows indicate the hot air stream of the autoclave. The sensor connected to channel 3 is placed on the center of the panel and the
other sensors each positioned a quarter of the width or respectively length from the border. As mentioned before, only four of the five sensor pairs could be connected and used at the same time. All four plots show a similar course. As in autoclaves the heat transfer is realized by convection of the circulating hot air, the temperature distribution can be very inhomogeneous. In consequence the cure progress can differ significantly in function of the location. This can be found in the plot of CH01, which is the furthest sensor point from the hot air entrance and where the cure progress is delayed. The temperature was measured on the bottom side of the tool at two locations. One thermocouple was applied near the sensor CH01 and another one near CH05. As the thermocouples were placed on the outer surface, the difference is minor (Fig. 6).

For a more detailed demonstration of the result’s analysis, the graph of CH05 was split into two parts with the addition of the signal amplitude (Fig. 7 and Fig. 8). In the very beginning of Fig. 7 the signal is shifting significantly, meaning a drop of the time-of-flight, in the first minutes while the signal amplitude is increasing. Both are caused by building up the autoclave pressure leading to compressing the laminate and thus decreasing the laminate thickness and propagation path length of the ultrasound waves. In the following the tool and laminate are heated up to 130 °C at a rate of 2 K/min until approximately 60 minutes of the process time. Due to the rise of temperature the resin’s velocity of sound decreases resulting in a rising time-of-flight while the amplitude is increasing. After 60 minutes the first temperature dwell step is reached enduring until 350 minutes after the process start. During this stage the ultrasound time-of-flight first starts to decrease progressively and then slows down until it reaches a constant level correlating with the cure progress.
Arising at about 170 min, the local minimum of the ultrasound amplitude is also a characteristic phenomenon and linked to the vitrification. Due to the high impulse frequency (about 3 MHz) the vitrification occurs prematurely in comparison with other measurement methods like DMA (working in the Hz range). The glass transition temperature is shifted by approximately 7 K per frequency decade [14]. A more suitable point for determining the point of vitrification suggested by McHugh is the intersection of two tangents. The first is placed on the inflection point and the second on the asymptote of the time-of-flight course. The application of this method concludes that the resin vitrificates at about 240 min (Fig. 7). Due to the vitrification the cure reaction slows down drastically.

Starting from 350 min the temperature is increased to 180 °C resulting in further decrease in sound velocity (Fig. 8). By increasing the temperature the cure reaction is reactivated, so during the second dwell step another asymptotic decrease of the signal arriving time can be observed. The drop of signal amplitude during the heat phase can be explained by the different heat expansion of tool and cover plate compared to the prepreg, which may affect the acoustic coupling. The same effect can be seen in CH01, as the signal amplitudes of CH03 and CH07 are increasing significantly like observed during the first heat phase.

During the cool phase beginning at 500 min the sound velocity of the resin increases again resulting in a decline of time-of-flight until the signal is cut off. This is again due to the weakening acoustic contact between the cover plate and composite part caused by the different thermal expansion, which can also be seen in all four plots. Similar to the second heat phase the signal of CH03 and CH07 stay in contact with the cover plate for a longer time as the other two sensors CH01 and CH07. As CH01 and CH07 are placed further from the cover plate in the same direction as the fibers the highest difference in thermal expansion takes place at their locations.

This detailed analysis demonstrates clearly the value and potential of ultrasound for process monitoring, optimization and control. Throughout the trials, different process cycles were performed and monitored from which the following cycles were designed.

First the process described by the data sheet was performed as the reference (MTM 02). In this process the cure reaction does not stop in the first dwell step at 130 °C enduring 2 hours before the heat ramp. In the second dwell step at 180 °C the reaction proceeds only until an overall process time of about 290 min, 60 minutes before the actual end of the dwell step.

In the first temperature step it is usually not intended to reach vitrification, only gelation at a low reaction rate in order to limit residual stress [15]. Unfortunately, it is not possible to determine the exact gelation point by ultrasound [14]. Correlation measurements between rheology and ultrasound let assume that the gelation point occurs between the onset and inflections of the time-of-flight curve. The correlation was performed in a measurement setup, where both rheological and acoustic parameters of the curing resin can be examined simultaneously [11,16]. The results from this study have not been published yet, but several authors found comparable results [17,18] and also McHugh’s results suggest this approach, where the onset occurs at a constant degree of cure of about 35 %, as well as the point of gelation at about 60 %. The onset can be constructed by the intersection of a tangent at the area of low change in time-of-flight and a tangent in the inflection point similar to the tangent method for determining the point of vitrification. As Fig. 9 shows, the length of the first dwell seems long enough for gelation and the inflection point is reached at the end. Therefore, the target of reaching gelation seems to be fulfilled.

In regard of optimizing the process towards productivity, the standard process could be shortened by approximately one hour in the second dwell step. The standard process took 420 minutes including cool down, hence the cycle duration could be reduced by 14.3 % and by 18 % before the cool phase.
In the trial this productivity-optimized standard process was not yet performed, as optimization through single dwell step processes and the optimization of quality were addressed first. In the test cycles of MTM 03 and MTM 04 the temperature was held at 180 °C for 2 and 4 hours. In the cure monitoring results the high cure rate provoked by skipping the first dwell at 130 °C becomes visible by a very sharp time-of-flight shift peak after about 80 minutes (Fig. 10). Until this point the effect of temperature on the time-of-flight is dominant, but then the opposing effect of the high cure rate leads to an abrupt drop of the signal arrival time. Also the sharp negative peak of the signal amplitude indicates the fast cure. Based on these observations an important heat release can be expected. This is also indicated by the numerous kinks in both curves and the second negative amplitude peak. This can consequently result in temperatures much higher than 180 °C inside the laminate and hence thermal damage of the polymer matrix. If this is the case it would be necessary to lower the heat rate or return to include a low temperature dwell step. Regarding the duration the 4-hour-process could be reduced by about 45 minutes.

In MTM 05 and MTM 06 processes with a single dwell step process (180 °C) were performed. During the process of MTM 05 the temperature was held for 8 hours and the gained cure monitoring results used for an optimized process in MTM 06. It can be seen in Fig. 11 that the time-of-flight curve of MTM 05 does almost not change for about 200 minutes before the end of the process and thus its duration can be reduced significantly, which was realized in MTM 06. The same duration was used for MTM 07 to which a second dwell step at 180 °C of 2 hours was added. The purpose of the latter is to examine if higher mechanical properties can be achieved.

### 5.2 Glass transition temperature

Samples were extracted from the test panels and tested by Differential Scanning Calorimetry (DSC) for glass transition temperature $T_g$ and remaining reaction enthalpy $\Delta H$. For obtaining the reaction enthalpy the samples were heated at a rate of 1 K/min to 230 °C. The results showed almost no released heat and therefore its value was not determinable.

The glass transition temperature was measured at a heat rate of 10 K/min from 30 to 240 °C and analyzed by the midpoint method in accordance with DIN 65467. Three samples of every panel were tested showing high reproducibility (Fig. 12). The glass transition temperature is a good indicator for the polymer network density and underlies sensitive change in the range of high degrees of cure.

The test panel MTM 02 produced after the process cycle described in the data sheet achieved a $T_g$ of 191.6 °C, while in MTM 03 the glass transition temperature was only 3.8 K lower (187.8 °C), although the process was reduced to the second dwell step of the standard cycle.

The highest glass transition temperatures were reached by the processes MTM 04 (195.8 °C) including the longest cure time at 180 °C and MTM 07 (194.8 °C) with a long first dwell step of 4.7 hours at 130 °C and then 2 hours at 180 °C. As expected the two cycles MTM 05 and MTM 06 with a cure temperature of only 130 °C lead to considerably lower glass transition temperatures (150.9 and 143.4 °C), indicating that the limit value of low change in time-of-flight for terminating the
process was chosen too high and the process was terminated prematurely.

Fig. 12. Glass transition temperatures of the test panels

Regarding the glass transition temperatures the best process cycle aiming at high productivity seems to be a single dwell step at 180 °C between 2 and 4 hours depending on the targeted glass transition temperature. On the other hand these processes work with high reaction rates throughout the complete duration. This can lead to residual stress, partial thermal degradation by exothermic effects and may affect the fiber-matrix-interface, which is not reflected by glass transition temperature measurement.

5.3 Three point flexural test

The prepreg panels were first inspected visually and by ultrasound scan for voids or other irregularities and then cut into coupons for preparing the specimens for tension, pressure, interlaminar shear and flexural tests. As mentioned before only the flexural tests were performed to this point.

The flexural three point tests were performed after DIN EN 2562 with specimen dimensions of 100 x 10 mm² with 10 specimens for each test panel. The obtained flexural strain, strength and modulus are represented by their median values for each test panel in Fig. 13, Fig. 14 and Fig. 15. The median was chosen over the mean value to reduce the influence of outliers. Also the bar plots are scaled in function of the range of values and standard deviation for better visual comparison. Although double the number of the minimum required specimens was tested, the results are relatively wide spread. Hence only tendencies between the flexural properties of the panels in function of their different process cycles can be derived. Nonetheless, observations similar to glass transition temperature can be made.

Likewise as the glass transition temperature the process MTM 03 reaches a lower property level than the standard process, while in MTM 04 higher flexural strain, strength and modulus were achieved. The results seem not to support the assumption that
thermal damage by exothermic heat release or high residual stress could have been caused by the fast processes. They confirm on the other hand the observations from the previous chapter that regarding the optimization of productivity while reaching the same properties from the standard process, the process should consist of one single temperature dwell step at 180 °C with duration between 2 and 4 hours. The optimal duration suggested by the cure monitoring system was about 3.25 h and has to be confirmed in a future test process.

Considering quality optimization on the other hand, by far the highest values were attained by MTM 07, while the glass transition temperature of MTM 04 is at the same level. As intended the first long dwell step at low temperatures for slow reaction rates seems to reduce residual stress leading to increased mechanical resistance.

The two low temperature processes MTM 05 and MTM 06 result as expected in low flexural properties. The flexural strength of MTM 05 is slightly higher than the one of MTM 06 while the flexural strength is equal. No satisfying explanation for the unexpected high flexural modulus of MTM 06 could be found, but high measurement scattering. Regarding flexural strain and strength the early process termination guided by the cure monitoring system seems admissible in contrast to the glass transition temperature.

6 Conclusion

Unidirectional prepreg test panels were produced by six different autoclave process cycles using cure monitoring with the aim of optimizing the process regarding productivity and quality. The process profile described by the data sheet served as reference and was used to derive the process variations. The cure progress was monitored by tool mounted ultrasound sensors at four locations. The cure monitoring results were used to optimize the process cycles in means of providing a criterion for terminating dwell steps. The panels were tested for glass transition temperature and flexural properties. For productivity optimization in terms of reaching the same properties as in the reference process, temperature profiles consisting of one single dwell step at 180 °C have been found as the most suitable. Two of those processes with each 2 and 4 hours of duration have been performed, reaching respectively slightly lower and higher property levels. The cure monitoring results suggest a duration of 3.25 hours for complete cure. By the latter the overall autoclave process would be reduced by 16.6 %. The cure monitoring results of the standard process suggests also a reduction of about 14.3 %. Both optimized processes will be examined by further tests. It has to be stated that these fast processes are based on high reaction rates throughout the whole process which risks high exothermic heat release. This could lead to thermal degradation of the polymeric matrix, especially for parts with high laminate thickness, where the heat cannot be transferred to the part surface at a sufficient rate.

The optimization of laminate quality can be realized by a first dwell step at low cure temperature (130 °C) until the cure monitoring system indicates a limit cure rate followed by a dwell step at 180 °C terminated as well by cure monitoring guidance. This process on the other hand results in a significant increase of the overall process by about 40 %, but also a significant increase in flexural properties.

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8 References

[1] F. de Wit, Control of setting compound carbon/glass fiber reinforced plastics materials, comprises sensors in resin layers during hardening process to monitor dielectric characteristics to determine setting action.


