SENSOR-BASED PROCESS MONITORING OF IN-SITU POLYMERIZATION IN T-RTM MANUFACTURING WITH CAPROLACTAM

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ABSTRACT

In the context of process digitalization for automotive lightweight structures, the impregnation with caprolactam and the polymerization process to polyamide 6 have been validated. This paper especially presents the results of the sensor-based process monitoring of a thermoplastic compression RTM process. The sensor data of four different sensor types is discussed, as there is pressure, temperature, ultrasonic and dielectric sensors. As a result, the knowledge on the processing of caprolactam and the machinery is now suitable for a sensor-based closed-loop process control system.

1. INTRODUCTION

In the context of future manufacturing technologies for composite lightweight structures, there is a strong need for sustainable and efficient, but also easily operated solutions. Especially the electromobility sector has high potential for innovative materials, smart manufacturing processes and high production rates. However, state of the art production technologies for automotive composites (e.g. thermoset RTM and back injection moulding) already involve high automation and quality standards. Competitive and innovative approaches therefore afford new material combinations and optimized conditions for process control and quality assurance. These challenges have been intensively investigated in the joint research project “Composites for Sustainable Mobility – CosiMo*”.

1.1 Project CosiMo

The aim of CosiMo is to demonstrate and validate the manufacturing process of an automotive demonstrator composite structure. Therefore, the advantages of an off-the-shelf resin transfer moulding (RTM) process are combined with the advantages of thermoplastic matrix systems in a thermoplastic RTM (T-RTM) process. In particular, the state-of-the-art, cost-intensive manufacturing of fibre-reinforced polymer (FRP) components is optimized both economically and ecologically. Addressing these challenges, the key topics of the CosiMo project are

- the impregnation of glass fibre nonwoven materials and in-situ polymerization of ϵ-caprolactam to polyamide 6 (PA6),
- the analytic material characterization of fibre materials and matrix system,
- the development and validation of an intelligent RTM mould based on an integrated process monitoring system,
- a central data management system bringing together machine and sensor data,
- the process data-driven development of virtual models of machines and processes using process simulation software and methods of machine learning.

[2]This paper presents results of the joint research project CosiMo (Composites for sustainable Mobility) funded by the Bavarian government under the Campus Carbon 4.0 program.

All these key topics have been validated on a demonstrator, of which development and design also have been part of the project. A more detailed overview of the project CosiMo was presented by Stieber et al. [1] and Beyrle et al [2]. The present paper mainly focuses on the sensor network and the sensor-based data analysis describing the injection and the polymerization reaction process.

1.2 In-situ polymerization of caprolactam

The in-situ polymerization of ε-caprolactam (CL) to polyamide-6 (PA6) takes place via ring-opening anionic polymerization. In this process, strong bases, such as alkali metals, act as so-called initiators and form free CL anions. These CL anions carry out a nucleophilic attack on another CL monomer, resulting in ring opening and the formation of an amine anion. Due to the higher basicity of the amine anion compared to the CL anion, a new CL anion and aminoacyllactam are formed by rapid proton exchange. Chain growth occurs by repeated nucleophilic attack of the CL anion on the endocyclic carbonyl group of the non-ionic growth centre. The CL anion is reformed after each growth step.
Polymerization initiated by CL anions alone requires high activation energies and proceeds slowly. The introduction or in-situ generation of N-acyl lactam structures that act as growth centres can lower the activation energy and increase the rate of chain growth. These N-acyl lactams are called activators.
The activated anionic polymerization of caprolactam (CL) to polyamide-6 (PA6) is characterized by short reaction times in a few minutes and low reaction temperatures between 140 - 180°C. It depends on the choice and concentration of activators and initiators. A major advantage of polymerization below the melting temperature of PA6 (melting point: 223 °C) is, that it is accompanied by rapid solidification due to simultaneous crystallization. The final product has improved polymer properties, such as a high crystallinity of up to 50% and a high average molecular weight in the range of 10^4 to10^6 g/mol. Furthermore, a high conversion between 96-99% is possible, which means that the residual monomer content is low. There are different methods for determining the residual monomer content of PA6. Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy gas analysis offers a fast and precise possibility [3].
The described properties together with a low melting temperature of ε caprolactam of 69°C and a low viscosity of about 5 mPa·s at 100°C make the anionic polymerization well suited for various technological applications, such as the T-RTM process.

1.3 3K Thermoplastic compression RTM process

The manufacturing process under investigation in the CosiMo project is a 3K thermoplastic RTM (T-RTM) process. Based on the CAPROCAST technology, patented by Tecnalia, Spain, liquid caprolactam is injected and polymerized to PA6 [4]. Therefore, an injection machine by KraussMaffei Technologies, Germany, has been integrated into the DLR research facilities in Augsburg, Germany. Basically, caprolactam as monomer and additives, as there are initiator and activator, are separately pre-processed. Afterwards they are dosed, mixed and injected according to the desired mixing ration and processing conditions with a mixing head directly mounted to the RTM tooling. The mixture of the three components of the polymerization reaction is characterized by a high amount of caprolactam and low volumes of the additives. This is why the mixing head resists limited pump pressures compared to high-pressure RTM processes. As a result, a compression T-RTM technology has been used, where a gap between lower and upper mould is applied during injection. A detailed description of the machinery and the process design was given by Stefani et al [5]. They described the analysis of temperature and pressure sensors based on generic flat PA6 panels reinforced with glass fibre and carbon fibre textiles.
In a subsequent test series, a complex manufacturing demonstrator has been validated in a comprehensive evaluation of temperature, pressure, DEA and ultrasonic sensors. This approach and the results are discussed in the following.

2. EXPERIMENTATION

The major goal of the test series with the complex manufacturing demonstrator is strengthening the understanding of the processing of caprolactam to PA6 under industrial conditions. Therefore, several

chicanes were addressed during the part design as there are textile reinforcements, metal inserts, thickness variations or areas with pure matrix. As textile reinforcements, glass fibre nonwovens and glass fibre non-crimp fabrics are used. Fibres of both materials feature a reactive size, especially adjusted to the polymerization reaction.

2.1 Sensor systems

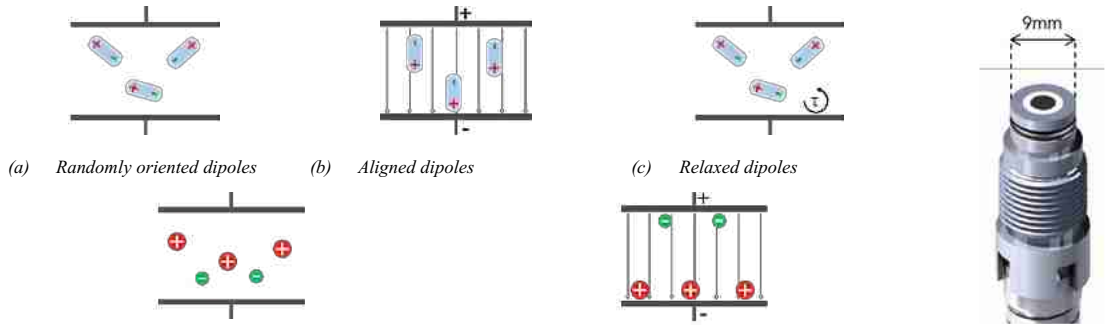
For a comprehensive investigation and analysis of the injection and the polymerization, a sensor network consisting of several sensor types for flow front and polymerization monitoring was developed. In total, 74 sensors were integrated into the mould (57 x ultrasonic, 8 x DEA, 4 x temperature, 4 x pressure/temperature, 1 vacuum).

2.1.1 Pressure and Temperature sensors

Temperature sensors can be used for flow front monitoring in the present project according to a temperature difference between the injected liquid caprolactam (approx. 120 °C) and the RTM mould (approx. 160°C). The arrival of the flow front can also be detected by pressure sensors according to a pressure difference between the injected caprolactam (approx. 1.5 bar) and the mould (approx. 0.02 bar). Furthermore, previous investigations showed characteristic profiles of temperature and pressure signals during the polymerization process. This is caused by the exothermic reaction and shrinkage effects. Additionally, temperature and pressure sensors are suitable for monitoring the reproducibility and the homogeneity of the process conditions. The in-mould pressure is detected by KISTLER 4001 pressure sensors which also offer an integrated temperature sensor. Three in-mould temperature sensors of KISTLER 6192 BG are used as well. Another temperature sensor (GF-7103, Graeff) is mounted to the lower mould without contact to the cavity. A vacuum sensor (type KISTLER 4080B130-LC) measures the applied vacuum.

2.1.2 DEA sensors

The polymerization and crystallization process have been monitored by the dielectric analyser NETZSCH DEA288 Ionic with some enhancements regarding sensor concept and new software capabilities for a real-time determination of the degree of conversion from ε-caprolactam to PA6 leveraging machine learning. The minimum data acquisition rate is less than 5 msec. The dielectric measurement principle is based on the excitation of the polymer with an alternating electric field. Due to the penetration, dipoles and free charge carriers, respectively partially charged smaller molecules will move towards the opposite charged electrode (see Fig. 1).



(a) Randomly oriented dipoles *(b) Aligned dipoles* *(c) Relaxed dipoles*

(d) Freely moving charge carriers, respectively partially charged small molecule groups *(e) Accumulated charge carriers* *(f) DEA sensor, NETZSCH*

Fig. 1: Polymer response during a dielectric measurement and figure of a Netzsch DEA sensor [6]

As a sensor, a monotrode concept has been chosen. This concept has the ability to measure through the sample thickness (bulk field) and with a limited penetration depth into the sample and back (fringe field) at the same time. In addition, this sensor also measures the temperature and is, due to a special coating design, capable of measuring the polymerization of ε-caprolactam – also in the presence of

carbon fibers. The sensor – from its outer dimensions identical to a Kistler 4001A or 6161A pressure sensor - can withstand permanent temperatures of up to 280°C and pressures of more than 300 bar.

2.1.3 Ultrasonic sensors

For flow front monitoring, 57 ultrasonic sensors, 10 of which operating in transmission mode, are integrated into the mould at a distance of 20 mm from the cavity's surface. The schematic design of the sensor is shown in Fig. 2 (a) consisting of a PZT disk from PICeramic (type PRYY+0227) with dimensions of 10 mm x 1 mm and a nominal resonant frequency of 2000 kHz. To insert the sensors into the mould, steel sensor holders were fabricated to which the piezo ceramic disks were bonded using a 3D printed connector as a damping compound, while constant contact pressure is applied by a spring-loading. The principle of the measurement is shown in Fig. 2 (b), illustrating the influence of the flow front on the acquired ultrasonic signals in reflection and transmission.

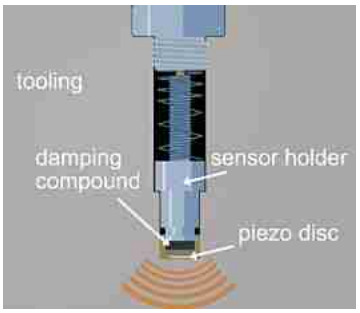


Fig. 2 (a): Main components of an ultrasonic sensor integrated into the metal tooling.

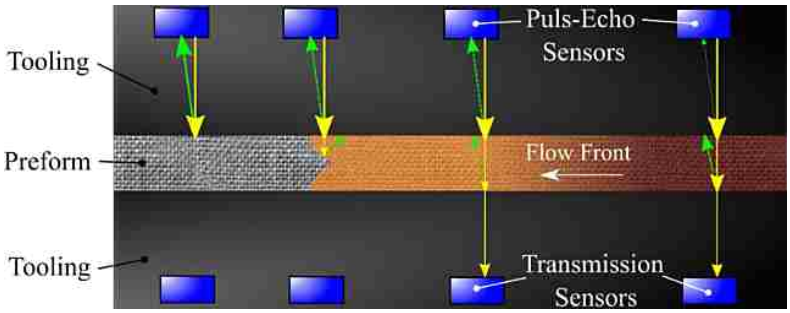


Fig. 1 (b): Schematic illustration of the flow front detection via ultrasonic sensors with yellow and green arrows indicating transmitted and reflected waves.

An external control board drives the pulser and performs analogue pre-processing of the signals. The pulser consists of a MOSFET driven spike pulse generator [7] and an expander-limiter design [8] to excite the sensors with a 12 V spike pulse of about 300 ns length without overloading the preamplifier. The acquired echo signal is filtered with a 1 MHz high-pass filter and amplified by 40 dB using an instrumentation amplifier (AD8421 from Analog Devices). This signal is then digitized at 20 MS/s using a streaming system (M2p.5923-x4, Spectrum Instrumentation GmbH).

2.2 Sensor network and data acquisition system

Since data is provided from many different sensors, it is important to create a common time base for all sensor signals. Within the CosiMo project, the software ibaPDA from iba AG, Germany has been selected for this purpose. This software is able to retrieve sensor data from a broad variety of systems such as PLCs and store them in a time series database.
Besides the sensors described in section 2.1, also data from the Wickert hot press and the KraussMaffei RTM machine are acquired and logged. Both systems are equipped with a Siemens S7-300 PLC which can be accessed using ibaPDA. For best performance, a small software component has been installed on the PLC which actively transmits all sensor data using UDP packets to the central data acquisition station. This allows low latencies, low overhead and provides sensor readings in every PLC cycle.
The sensors described in section 2.1.1 are connected directly to appropriate input channels of a Beckhoff TwinCAT 2 PLC using EtherCAT. The DEA sensors described in section 2.1.2 are connected to dedicated evaluation unit provided by Netzsch, which internally logs the data and also provides selected values using analogue outputs (0V-10V). These analogue outputs are also connected to the Beckhoff PLC. The ibaPDA software acquires the current measurement values from the Beckhoff PLC using the ADS protocol and thus can store these values in the timeseries database as well.
The ultrasonic sensors described in section 2.1.3 unfortunately do not yet provide any external interface and thus are logged only in their respective evaluation unit and their data is included in the central timeseries database only after post-processing.

For synchronization of the different measurement and evaluation units, the Beckhoff PLC also generated trigger signals based on the current state of the process (using digital 24V or 5V trigger signals). Since no direct connection of the Wickert hot press (which is in charge of running the process) and the Beckhoff PLC exists and modification of the existing systems should be minimized, real-time data already acquired by ibaPDA is used for synchronization. The ibaPDA provides an OPC/UA server which is able to provide all current values. Using a small Java-based bridge between OPC/UA and Beckhoff ADS, the necessary values describing the current process state are mirrored to the Beckhoff PLC. Using these values, the trigger signals can be generated. By using the OPC/UA interface, no modification of the existing systems is required, however latency and jitter are introduced which must be considered. Since the trigger signals are generated early in the process long before fast processes happen, the latency and the jitter are tolerable.

3. RESULTS

Based on the process monitoring systems integrated into the RTM mould, the flow front propagation during the injection phase and the polymerization reaction have been investigated. The response of each sensor can be compared to the others, correlated with machine data and analysed with regards to the location inside the mould.

3.1 Flow front detection

3.1.1 Flow front detection with temperature and pressure sensors

When the liquid reactive mixture of caprolactam and additives arrives, the temperature inside the mould decreases due to the comparably higher temperature of the mould. The mould temperature varies between 160 °C and 170 °C. The caprolactam is heated up to approx. 120 °C. The temperature drop can be detected as shown in Fig. 3 (a) and thereby it is a valid indicator of the flow front arrival.

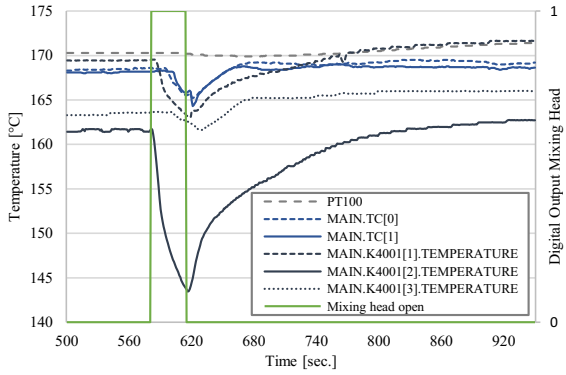


Fig. 3 (a): Flow front detection with temperature sensors

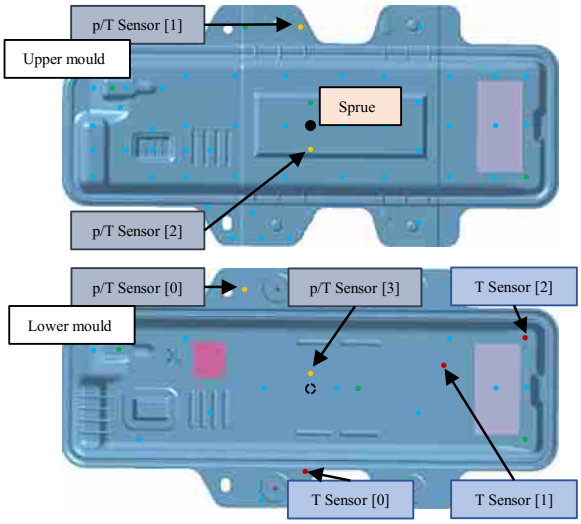


Fig. 3 (b): Position of the pressure and temperature sensors in the upper and lower mould

The higher the distance between the sprue and the temperature sensor, the later the temperature drop occurs and the lower the temperature drop is. For example, p/T sensor [2] is located close to the sprue in the upper mould (see Fig. 3 (b)). This leads to the highest temperature drop measured (Fig. 3 (a)). Compared to the presented results, pressure rise during arrival of the liquid reactive mixture was less sharp. Due to additional effects like fibre movement inside the dry preform during compression, the pressure signal does not show the flow front as precise as the temperature signal.

3.1.2 Flow front detection with ultrasonic sensors

The acquired ultrasonic signals are strongly influenced by the reflection conditions of the cavity's surface. This correlation can be used for a flow front detection. Initially, the reflective coefficient at the interface may be assumed to be $R \approx 1$ due to the rather poor coupling between the dry fibres of the preform and the tooling. However, the impregnation of the preform causes a significant rise in the preform's acoustic impedance, reducing R and thus allowing for a flow front detection via the noticeable decrease of the signal amplitudes. An exemplary set of acquired ultrasonic signals is shown in Fig. 4 (a). The main echo cascade in the pulse-echo and transmission signal stems from multiple reflections between the upper and lower mould surface, respectively. In Fig. 4 (b) the normalized magnitudes of the signal echo during entry of the cavity versus time of three sensors at different locations is plotted. The abrupt decrease of the signals upon flow front arrival is clearly distinguishable.

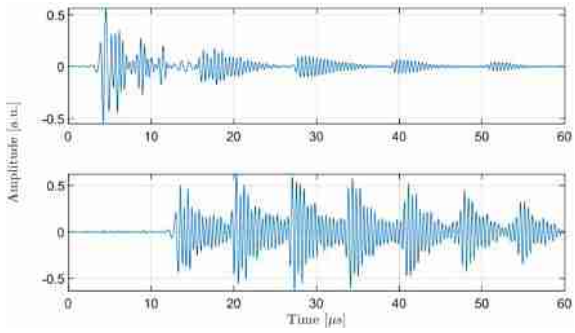


Fig. 4 (a): Ultrasonic signals. At the top, the pulse-echo signal, at the bottom the corresponding transmission signal.

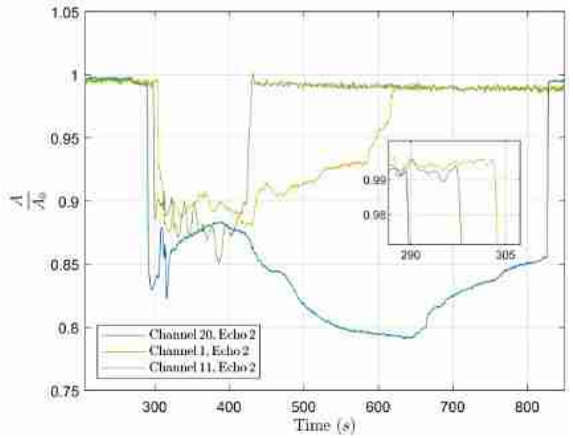


Fig. 4 (b): Normalized magnitudes of the 2nd main echo versus time with a closed up at the time of the flow front arrival.

Applying a magnitude drop to 95 % of the initial value allows for a flow front detection at the corresponding sensor position, yielding a maximum time of arrival up to 15 sec after the injection.
A return of the echo amplitude back to its initial value after some time, as observed with sensor 11 and 1 in Fig. 4 (b), may indicate a separation of mould and impregnated preform. Other explanations are a possible repercussion of the volume shrinkage or voids occurring during the polymerization. In contrast, the sharp rise in the signal of sensor 20 marks the end of the experiment, i.e. the opening of the mould.

3.2 Polymerization monitoring

After the injection of the liquid reactive mixture, the polymerization reaction immediately begins. The material conversion to PA6 has been extensively investigated based on the different sensor types.

3.2.1 Polymerization monitoring with DEA sensors

To monitor the conversion (alpha) during the polymerization from ε-caprolactam to PA6 and the subsequently following crystallization, the dielectric signals from the sensors have been combined with a reaction kinetic model, based on quasi-isothermal differential scanning calorimetric investigations. Deviations due to temperature have been considered and a huge number of datasets has been simulated. All data has been combined within a machine learning model that offers the possibility to create material quality data based on the dielectric sensor signal in real-time during production. In addition, the developed software environment is capable of simulating error states once a failure during production occurred and was told to the dielectric measuring system. As a consequence, a continuously running reinforcement learning with the dielectric sensor data of each manufactured part can be performed to

ensure an enhancement of the used model and to increase the efficiency of the production line from time to time.
In Fig. 5 the measured as well as the machine learning based degree of conversion (alpha) for one of the produced components within the CosiMo project is represented. One can observe a sharp decrease of the ion viscosity signal at around 4 minutes that indicates the flow front detection. Around 4.5 minutes, the minimum ion viscosity and therefore the best flow behaviour of ε-caprolactam has been reached before the polymerization starts. Between 4.5 and 7 minutes a wave can be observed during the polymerization that could be based on two effects:

- a temperature variation as it could be observed in the graph or
- a change in the reaction mechanisms during the polymerization as a consequence of the switch from polymerization to crystallization.

The machine learning model that is calculating the degree of conversion is working in the following:

1) Recognizing the minimum ion viscosity.
2) From the minimum in ion viscosity, data for two more minutes are recorded to see the material behaviour and to have a chance to adapt to changing process or material conditions.
3) Calculating the prediction for the expected future ion viscosity and temperature evolution as well as predicting alpha till the end of the process.
4) Repeating the prediction of all signals from time to time until reaching a probability high enough that the model assesses the prediction to be reliable.

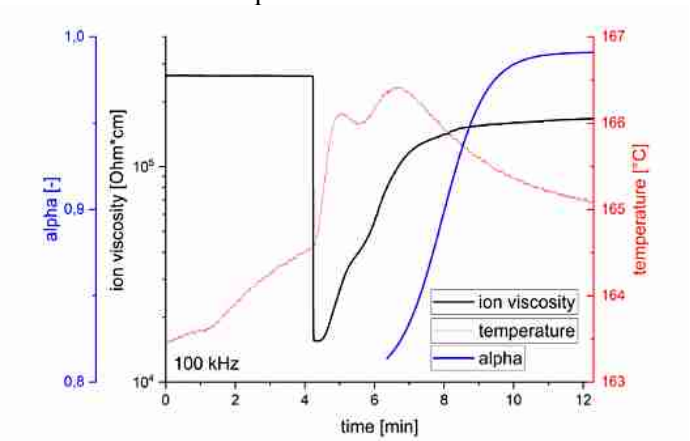


Fig. 5: Representative polymerization monitoring and calculation of the quality criterion degree of conversion (alpha) for one of the manufactured components within the CosiMo project.

Within the project, the functionality of the setup consisting of sensor data, reaction kinetics and software with machine learning capabilities has successfully been proven. Based on the data generated during the production of the component represented in Fig. 5, a degree of conversion of 98.5 % as the target alpha could be reached at 10.1 minutes, respectively 5.7 minutes after injection. This value fits to the expectations and has to be further correlated to and evaluated by post-process laboratory measurements.

3.2.2 Polymerization monitoring with pressure sensors

The pressure signals describe the characteristic mechanisms of the compression T-RTM process induced by the machines (e.g. compression) and the material conversion (e.g. shrinkage). According to Fig. 6, pressure slightly rises during injection and highly increases during compression, when the mould is closed. Pressure sensor No. 2 is located close to the sprue in the upper mould, while pressure sensor No. 3 is located on the opposite side of the preform in the lower mould. After compression phase, these sensors are only separated by the matrix and the laminate including a foam core in this area of the part. It can be seen, that the sensor on the lower side (No. 3) shows a significant second peak. Assuming, that the impregnation is finished at that time, this effect may be caused by stresses inside the laminate and especially inside the foam core. This theory is underlined by similar effects in the outer region of the part (see also sensor No. 1). When comparing the pressure signals with a qualitative description of the

ion viscosity of the DEA sensor, one may conclude, that the pressure reaches the starting values when the polymerization comes to an end at approx. 850 sec. This correlates with the results in chapter 3.2.1.

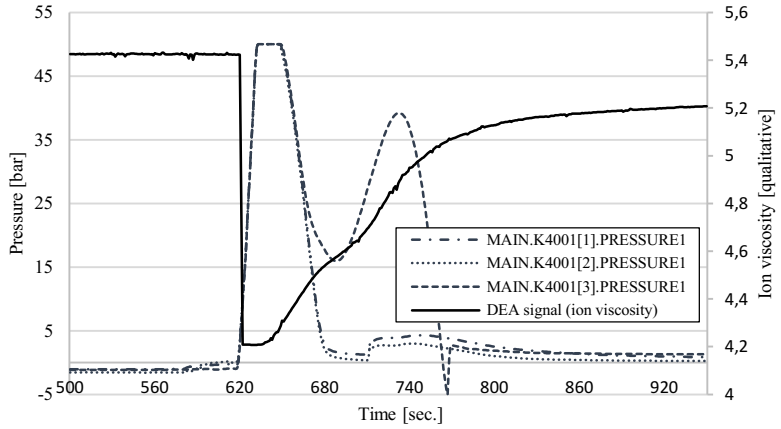


Fig. 6: Comparative demonstration of pressure and ion viscosity

3.2.3 Polymerization monitoring with ultrasonic sensors

Based on the ultrasonic signals it may be possible to track the degree of polymerization at the sensor location over time. Since the acoustic pressure p is proportional to the ultrasonic signal's amplitude A, the ratio of the echoes amplitude before and after the preform impregnation is given by

$$\frac{A_1}{A_0} = \frac{R_{mould,part}}{R_{mould,air}} \approx R_{mould,part} \text{ with } R_{mould,air} \approx 1.$$

The ratio only depends on the reflective index $R_{mould,part}$ approaching a constant value as the polymerization progresses. Thus, an advanced state of the polymerization should result in a convergence of A_1/A_0. An example of the behaviour of A_1/A_0 over time is illustrated in Fig. 7 (a). To monitor the state of the polymerization progress, the degree of the saturation is to be assessed. For this purpose, the derivative of A_1/A_0, is shown in Fig. 7 (b). A value approaching "0" may therefore indicate a rather advanced polymerization as observed in this case.

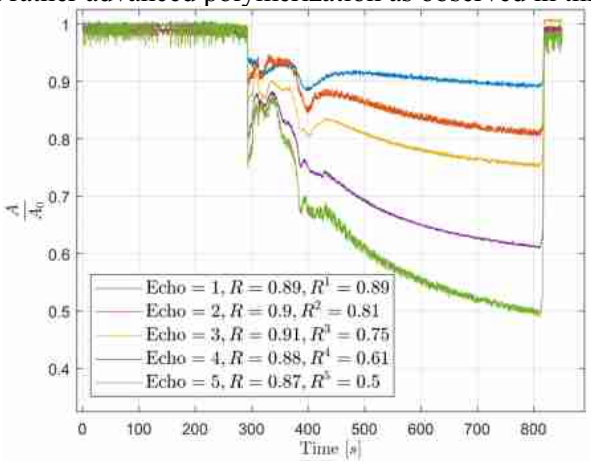


Fig. 7 (a): Magnitude of the main echoes versus time with R extracted from the value $\frac{A_1}{A_0} = R^n$ *just before the sharp rise of the signal with* n *as the number of the ultrasonic wave's reflection at the tooling's upper surface.*

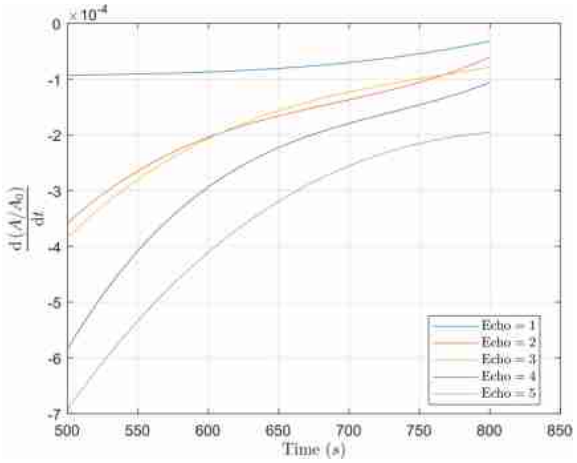


Fig. 7 (b): The corresponding derivatives obtained from a 4th-order polynomial fit applied to the time span from 500 to 800 seconds after the start of the measurement.

Furthermore, via the transmission signal, it is possible to extract the travel time $t_{preform}$ for the ultrasonic waves to pass through the impregnated preform. This may be proved to be valuable for the polymerization monitoring since the speed of sound $c(t)$ obtained through $t_{preform}$ is expected to be linked to the degree of polymerization. When flattening $c(t)$ over time this may indicate a saturation of the polymerization. Thus, the time between the thorough wetting of the preform at the sensor's location until the completion of the polymerization may be approximated by $\Delta t \approx 240s$. Nevertheless, since this evaluation requires the transmission mode, further studies will focus on the exploitation of the A_1/A_0 ratio to evaluate the degree of polymerization.

4. CONCLUSIONS

The major goal of the Project CosiMo to evaluate the polymerization reaction of caprolactam to PA6 by an intelligent RTM mould and a central data acquisition system has been successfully accomplished. Sensors measuring temperatures, pressures, acoustic echos and dielectric response have been combined to a comprehensive sensor network. Based on this network, flow front, polymerization reaction and further characteristic material effects during the transition from a liquid monomer to a solid thermoplastic polymer have been investigated. The presented results allow a fundamental process understanding on the one hand and new opportunities to optimizing cycle time and quality assurance on the other hand. Nevertheless, industrial manufacturing processes afford easy-to-operate solutions and only a minimum number of integrated sensors used in a close-loop control system. These challenges need to be addressed next.

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