Ph.D. Thesis

Micro Injection Moulding for Micro Fuel Cell Production

July 2016

Timo Wöhner

Department of Mechanical Engineering
Technical University of Denmark
Preface

This thesis was composed as one of the requirements of the Ph.D. degree at the Technical University of Denmark (DTU), Kongens Lyngby, Denmark.

The work presented in this thesis has been carried out between December 2012 and June 2016 at the Department of Mechanical Engineering (MEK) at DTU under the supervision of Prof. Hans Nørgaard Hansen, Associate Professor Guido Tosello and Associate Professor Aminul Islam.

From June to July 2015, five weeks were spent at the Centre for Polymer Micro and Nano Technology at the University of Bradford, Bradford, United Kingdom, under the supervision of Dr. Ben Whiteside.

I would like to thank all my supervisors for their great support and their contribution to this work. My special thanks go to Prof. Hans Nørgaard Hansen for the fruitful discussions, the constructive feedback during this period and for giving me the opportunity to conduct the Ph.D. programme at DTU.

Furthermore, I would like to thank Dr. Ben Whiteside and his team at the University of Bradford for the perfect organization and the great hospitality during my external stay there. The experiments conducted during this period and Dr. Ben Whiteside’s feedback were a significant contribution to this work.

The funding of this Ph.D. project by DTU and the financial support by the Danish Innovation Consortium “NanoEnergi” (Development of Direct Methanol fuel cells) is gratefully acknowledged.

Kongens Lyngby

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Timo Wöhner
Abstract (English)

In this PhD-project, the development of injection moulded containers for Direct Methanol Fuel Cell (DMFC) systems is described. This developing work aims at DMFC-Systems for the application in hearing aid systems, which results in a variety of requirements and specifications for the design of the system as well as the manufacturing process.

Beginning with an introduction to different fuel cell systems and the suitability of the DMFC to power small portable electronic devices, the background knowledge is presented to provide an understanding of the challenges for the injection moulded container from both the fuel cell system and the manufacturing side.

The implementation of the transfer of the design of an existing fuel cell container made out of metal comprises the selection of a suitable process and of the materials, which are compatible to both the process and the functionality of the final part as well as the mould design.

The experimental part deals with the suitability of the material combination of the chosen micro film insert moulding process. A phenomenon which was found in this process is the occurrence of blisters in the surface-layer of the chosen dual layer film insert for certain combinations of the processing parameters. These blisters can deteriorate the functionality of the film insert in the application in the fuel cell container and even lead to fatal failure of the container in case of a complete delamination of the film insert.

A detailed investigation on the reasons for the blister formation was conducted. During these investigations, different techniques such as in-process monitoring, computed tomography (CT) scans, surface metrology and process simulations were employed.

These investigations revealed that the blister creation is related to the shrinkage of the overmoulding material during the cooling phase of the injection moulding process cycle. The biggest influence on the blister creation was found in the process parameters melt and mould temperature. A process window for micro film insert moulding with the chosen material combination was found, which led to the production of blister free surfaces. Therefore, the process was found to be suitable for the implementation of the chosen design. The measurement routine developed to characterize the blistered surface can be applied to define a suitable process window for similar production with other combinations of materials than the one presented in this work.

A mould based on a standard split-mould design was designed for the production of the fuel cell container. This design contained features to create a venting structure in the sidewall of the methanol container and a vacuum system for the fixation of the film insert.

Furthermore, injection moulding experiments for the fuel cell container were conducted. These experiments revealed problems with parts of the mould design, which were solved by a second iteration of the concerned mould part and by a change in the material of the film insert.
Finally, the successful production of the DMFC-container in a process suitable for cost efficient mass production could be achieved. A first test with the moulded containers showed insufficient methanol retention properties. Therefore, a redesign of the container will be necessary.
Resume (Dansk)

Dette PhD projekt beskriver udviklingen af sprøjtestæbning af containere til Direct Methanol Fuel Cell (DMFC) systemer. Arbejdet omhandler DMFC-systemer til anvendelse i høreapparater med de dertil hørende krav og kriterier i forhold til funktionalitet, størrelse, materialer og produktionsprocesser.

Baggrund og state-of-the-art beskriver forskellige brænsecellesystemer generelt og specifikt DMFC-systemer til brug i forbindelse med små, bærbare elektroniske enheder. Derudover beskrives udfordringer og muligheder ved sprøjtestøbning af små containere.

Udgangspunktet for arbejdet har været en lille metalcontainer som med succes har været anvendt til DMFC-systemer. Dette projekt har omhandlet materialevælg, procesvalg, værktojskonstruktion samt procesoptimering.


# Table of Contents

Preface ........................................................................................................................................ i
Abstract (English) .......................................................................................................................... ii
Resume (Dansk) ........................................................................................................................... iv
List of Figures ................................................................................................................................ vii
List of Tables ............................................................................................................................... x
List of Acronyms ......................................................................................................................... xi
List of Mathematical Symbols ..................................................................................................... xiii

1. Background and Objectives .................................................................................................... 1
   1.1 Introduction to fuel cell systems ....................................................................................... 1
      1.1.1 Fuel cell systems and their typical applications ....................................................... 2
   1.2 Objectives of the PhD-thesis ........................................................................................... 8

2. State of the Art and theoretical background ......................................................................... 10
   2.1 Direct Methanol Fuel Cells ............................................................................................. 10
      2.1.1 Working principle of a DMFC ............................................................................... 12
      2.1.2 Effects reducing the efficiency in DMFC systems ................................................ 13
   2.2 Injection moulding ........................................................................................................... 17
      2.2.1 Special moulding processes .................................................................................... 20
      2.2.2 Micro injection moulding ...................................................................................... 22
      2.2.3 Film insert moulding ............................................................................................. 24
   2.3 Injection Moulding Simulations ....................................................................................... 27
      2.3.1 Governing equations .............................................................................................. 28
      2.3.2 Modelling of material properties ............................................................................ 29
   2.4 Summary .......................................................................................................................... 39

3. Injection moulding concept and material selection ............................................................... 40
   3.1 Process selection ............................................................................................................. 40
   3.2 Material Selection ............................................................................................................ 44
      3.2.1 Membrane .............................................................................................................. 45
List of Figures

Figure 1: Refill process of the DMFC in the hearing aid [22] ................................................................. 7
Figure 2: Schematic of the fuel cell system (LHS) and the single components of the system with a metal fuel container (RHS): Fuel reservoir, gasket, membrane electrode assembly, anode cup, anode current collector and lid including cathode current collector (from left to right) [22] ............... 8
Figure 3: Schematic of typical components of a passive DMFC system .................................................. 12
Figure 4: Theoretical energy densities and specific energies for different fuels and batteries .......... 13
Figure 5: Schematic of an injection moulding machine .............................................................................. 18
Figure 6: Main steps in an injection moulding cycle .................................................................................. 19
Figure 7: Two different concepts for micro moulding machines: Wittman-Battenfeld “Micro Power” with small screw for plasticating and plunger for injection (left hand side, Picture from [132] ) and DESMAtec “FormicaPlast” based on two pistons (right hand side, picture from [133]) .................. 23
Figure 8: Plot for the shear rate dependency of the viscosity. Red line: Newtonian plateau, Blue line: Power-law region, Black line: Cross-WLF model .............................................................. 30
Figure 9: PVT-diagrams for an amorphous and a semi crystalline Polymer .............................................. 33
Figure 10: Morphology of a polypropylene micro plate. Picture from [78] .............................................. 36
Figure 11: Concept study for fuel cell container: a) 2K-foam moulding b) Insert-moulding c) Film insert moulding, Top row: Iso-view, middle: Cross-sectional view, bottom: Insert .................. 42
Figure 12: Contact angle vs. pore diameter for selected membranes ...................................................... 49
Figure 13: Membrane (left-hand side) and support side (right-hand side of a set of two pictures for each supplier respectively) ................................................................. 53
Figure 14: Permeability coefficients for CO₂ and O₂ .................................................................................. 58
Figure 15: E-modulus vs. density plot of suitable overmoulding materials ............................................. 61
Figure 16: Mould inserts. Left hand side: Insert for fixed half (CAD-model), middle: Insert for movable half, right hand side: Insert for movable half with inserted film insert (CAD-model) ....... 62
Figure 17: Mould for in-mould visualization. Picture courtesy of Dr Ben Whiteside, RKT Centre Polymer MNT, University of Bradford, UK ............................................................................................. 63
Figure 18: Setup for in-mould visualization. Picture courtesy of Dr Ben Whiteside, RKT Centre Polymer MNT, University of Bradford, UK ............................................................................................. 64
Figure 19: Disc-shaped FIM-part (Scale unit: cm) ..................................................................................... 64
Figure 20: Top: Part after moulding including sprue, runner, gate and untrimmed membrane (scale unit: cm) ..................................................................................................................... 64
Figure 21: Cad-model of the fuel cell container with according dimensions a) isometric-view, b) top view c) front view .............................................................................................................. 65
Figure 22: Exploded view of the CAD-model of the split mould, a) split, b) core insert, c) pin array, d) angle pins ....................................................................................................................... 66
Figure 23: Movable half of the split-mould for the fuel cell container ........................................... 67
Figure 24: Estimation for displacement at 0.5 bar overpressure ....................................................... 68
Figure 25: Estimation of von Mises stress at 0.5 bar overpressure ..................................................... 68
Figure 26: Different pin combinations for the creation of CO₂ venting holes ................................... 69
Figure 27: Fill pattern and Pressure at the switch over point. From left to right: Run 2, Run 7 and Run 30 (Processing Parameters can be found in the appendix) .................................................. 73
Figure 28: Blue frame: Different mesh size on movable mould half (green), moulding (blue) and film insert (purple). The white circle marks the position of the vent ......................................................... 74
Figure 29: Meshed part and film insert .................................................................................................. 75
Figure 30: Proportional distribution in the recess .................................................................................. 76
Figure 31: Thermal conductivity of "Generic PET", "Generic PP"(data from the AMSI 2016 Database) and air (data from [134]) ........................................................................................................... 77
Figure 32: Measurement area of 5 x 10 mm² on the membrane in the centre of the part (red area) .......................................................... 82
Figure 33: Measurements obtained with different objectives ................................................................. 83
Figure 34: Areal material ratio curve and according areal surface roughness parameter (Picture taken from [124]) .................................................................................................................. 85
Figure 35: Correlation between Spk, Smr1 and blistered surface (R denotes the DoE-run and P the part number) ........................................................................................................................ 86
Figure 36: CT-scan of a blister free part ................................................................................................. 87
Figure 37: CT-scan of blistered specimen .............................................................................................. 87
Figure 38: Pulled out fibre at a blister .................................................................................................... 88
Figure 39: Comparison of an unblistered part (left-hand side) to a blistered one (right-hand side) in the high-speed recording .............................................................................................................. 90
Figure 40: Simulated filling behaviour of Run 6 (left hand side), overlay of experimental video (right hand side) .................................................................................................................. 92
Figure 41: Degree of filling at certain times. Comparison between IPM-video (sequence on top) and Simulation (sequence at the bottom) for run 8 part 1 ................................................................. 93
Figure 42: Main Effects of chosen parameters on Smr1 .......................................................................... 95
Figure 43: Interaction of T_mould/T_barrel on Smr1 .............................................................................. 95
Figure 44: Residual analysis for regression model of Smr1 ................................................................... 97
Figure 45: Main effect plots for the within run variability for Smr1 ...................................................... 98
Figure 46: Interaction for the within run variability of Smr1 ................................................................. 98
Figure 47: Main Effects of the parameters on Spk .................................................................................. 99
Figure 48: Interaction of Mould Temperature and Barrel Temperature on Spk .................................... 100
Figure 49: Interaction of Barrel Temperature and Packing Pressure on Spk ....................................... 100
Figure 50: Interaction of injection speed and mould temperature ...................................................... 100
Figure 51: Residual Plot for Spk .......................................................................................................... 102
Figure 52: Main effects plot for the within run variability for Spk ....................................................... 103
Figure 53: Difference between the maximum injection pressures obtained from the experiments and the simulations .................................................................................................................. 104
Figure 54: Relative Deviation of the maximum injection pressure between measured and simulated values ................................................................................................................................. 105
Figure 55: Path plot of average volumetric shrinkage
Figure 56: Main effects plot for simulated average shrinkage
Figure 57: Interaction of barrel temperature and packing pressure on the simulated average shrinkage
Figure 58: Residual Plots for the regression model of the simulation results
Figure 59: Different mesh sizes in the multiscale mesh
Figure 60: Unfilled section in the sprue puller (Run 3)
Figure 61: Temperature (left-hand side) and pressure distribution during filling of the sprue puller
Figure 62: Filling sequence of the container
Figure 63: Re-melted area (From left to right): ~20 % of sidewall area (run 1), ~40 % (run 3), ~60% (run 5) and 100% (run 16)
Figure 64: Warpage in the container; left hand side box effect, right hand side: warpage in direction of the part height (y-direction). Warpage magnified by a factor of five in both pictures
Figure 65: Measurement points for part warpage; left hand side: warpage in z-direction, right hand side: warpage in x-direction
Figure 66: Main effects on simulated warpage in x- and z-direction
Figure 67: Cross-section of the core insert with vacuum channels (dimensions in mm)
Figure 68: Plug with laser-drilled micro-channels
Figure 69: Polymer filled vacuum channels (left hand side) and destroyed membrane due to melt penetration (right hand side)
Figure 70: Container moulded with SABEU-membrane and double sided tape: destroyed membrane (left-hand side), successfully moulded part (right-hand side)
Figure 71: Topographical picture of the CO$_2$ venting hole in a container with the SABEU-membrane
Figure 72: Successfully moulded container with Porex-membrane
Figure 73: Membrane fixated by vacuum system prior to moulding
Figure 74: Impressions on the film insert surface of a container moulded with the Porex PM22ST-membrane
Figure 75: Venting hole in container moulded with Porex-membrane
Figure 76: Container filled with methanol and sealed by a lid
Figure 77: Change in Methanol stored in the container over time
List of Tables

Table 1: Overview of the six fuel cell classes of major interest (data from [1], [3], [4], [6], [7]) ........ 2
Table 2: Symbols used in governing equations .............................................................................. 29
Table 3: Pros and cons for concept choice ....................................................................................... 44
Table 4: Different membrane types tested at Teknologisk Institut [99] ........................................ 48
Table 5: Methanol intrusion pressures ............................................................................................... 50
Table 6: Permeability coefficient for Methanol [93] ......................................................................... 59
Table 7: HSP for chosen Polymers .................................................................................................. 59
Table 8: Injection moulding parameters for DOE analysis ............................................................. 72
Table 9: Specifications of LEXT 4100 lenses .................................................................................. 82
Table 10: Lens comparison unfiltered .............................................................................................. 84
Table 11: Lens comparison filtered .................................................................................................. 84
Table 12: Moulding parameters to Figure 9 .................................................................................... 89
Table 13: MS-values for factors in the regression model for Spk ..................................................... 101
Table 14: Values of the investigated parameters ............................................................................. 111
Table 15: Process parameter for injection moulding of the fuel cell container. ............................. 121
List of Acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>µIM</td>
<td>Micro injection moulding</td>
</tr>
<tr>
<td>2K</td>
<td>Two component</td>
</tr>
<tr>
<td>ABS</td>
<td>Acrylonitrile butadiene styrene</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AFC</td>
<td>Alkaline Fuel Cell</td>
</tr>
<tr>
<td>AMSI</td>
<td>Autodesk Moldflow Simulation Insight</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of Variance</td>
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<tr>
<td>AOI</td>
<td>Area of Interest</td>
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<tr>
<td>CA</td>
<td>Contact angle</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer aided Design</td>
</tr>
<tr>
<td>CAP</td>
<td>Cellulose propionate</td>
</tr>
<tr>
<td>CHP</td>
<td>Combined heat and Power unit</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
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<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
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<tr>
<td>COC</td>
<td>Polycycloolefin</td>
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<tr>
<td>CT</td>
<td>Computed tomography</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of thermal expansion</td>
</tr>
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<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DMFC</td>
<td>Direct Methanol Fuel Cell</td>
</tr>
<tr>
<td>DOE</td>
<td>Design of experiments</td>
</tr>
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<td>DRIE</td>
<td>Deep reactive ion etching</td>
</tr>
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<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<td>ePTFE</td>
<td>expanded PTFE</td>
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<td>EVOH</td>
<td>Ethylene vinyl alcohol copolymer</td>
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<tr>
<td>FEA</td>
<td>Finite element analysis</td>
</tr>
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<td>FIM</td>
<td>Film insert moulding</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<tr>
<td>H₃PO₄</td>
<td>Phosphoric acid</td>
</tr>
<tr>
<td>HDPE</td>
<td>High density PE</td>
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<tr>
<td>HIPS</td>
<td>High impact poly styrene</td>
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<td>HSP</td>
<td>Hansen solubility parameter</td>
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<td>htc</td>
<td>Heat transfer coefficient</td>
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<td>IPM</td>
<td>In-process-monitoring</td>
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<td>K₂CO₃</td>
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<td>Potassium Hydroxide</td>
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<td>LDPE</td>
<td>Low density PE</td>
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<td>LiAlO₂</td>
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<td>LIGA</td>
<td>Lithographie, electroplating and moulding</td>
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<td>LLDPE</td>
<td>Linear low density PE</td>
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<tr>
<td>MCFC</td>
<td>Molten Carbonate Fuel Cell</td>
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<tr>
<td>MEA</td>
<td>Methanol electrode assembly</td>
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<tr>
<td>MEMS</td>
<td>Micro electro mechanical systems</td>
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<tr>
<td>MOR</td>
<td>Methanol oxidation reaction</td>
</tr>
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<td>MS</td>
<td>Adjusted mean square</td>
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<td>Na₂CO₃</td>
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<td>NO₂</td>
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<td>ORR</td>
<td>Oxygen reduction reaction</td>
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<td>PA</td>
<td>Polyamide</td>
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<td>PAFC</td>
<td>Phosphoric Acid Fuel Cell</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Meaning</td>
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<tr>
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<tr>
<td>PBT</td>
<td>Polybutylene terephthalate</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PCL</td>
<td>Polycaprolactones</td>
</tr>
<tr>
<td>PDA</td>
<td>Personal digital assistant</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene, Polyethylene</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton Exchange Membrane Fuel Cell</td>
</tr>
<tr>
<td>PET</td>
<td>Polyethylene terephthalate</td>
</tr>
<tr>
<td>PM$_{10}$</td>
<td>Particulate Matter with diameter below 10 µm</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly methyl methacrylate</td>
</tr>
<tr>
<td>POM</td>
<td>Polyoxymethylene</td>
</tr>
<tr>
<td>PP</td>
<td>Poly propylene</td>
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<td>PS</td>
<td>Polystyrene</td>
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<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
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<tr>
<td>PTMSP</td>
<td>Poly[1-(trimethylsilyl)-1-propyne]</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl chloride</td>
</tr>
<tr>
<td>PVDC</td>
<td>Polycaprolactones</td>
</tr>
<tr>
<td>PVT</td>
<td>Pressure Volume Temperature</td>
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<tr>
<td>RFID</td>
<td>Radio frequency identification</td>
</tr>
<tr>
<td>RTD</td>
<td>Retardation-induced temperature drop</td>
</tr>
<tr>
<td>SATP</td>
<td>Standard ambient temperature and pressure</td>
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<td>SiC</td>
<td>Silicon carbide</td>
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<tr>
<td>Smr1</td>
<td>Surface material ratio 1</td>
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<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cell</td>
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<tr>
<td>SPEEEK</td>
<td>Sulphonated polyether ether ketone</td>
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<tr>
<td>Spk</td>
<td>Reduced peak height</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>WAXD</td>
<td>Wide-angle X-ray diffraction</td>
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<td>WHO</td>
<td>World health organisation</td>
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<td>WRP</td>
<td>Warpage removal phenomena</td>
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# List of Mathematical Symbols

<table>
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<tr>
<th>Symbol</th>
<th>Meaning</th>
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<tr>
<td>( \Delta G^M )</td>
<td>Free energy of mixing</td>
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<td>( \Delta V_{act} )</td>
<td>Overpotential</td>
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<td>Area</td>
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<tr>
<td>( b_X )</td>
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<td>( c_p )</td>
<td>Thermal penetration</td>
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<td>( d )</td>
<td>Specific heat capacity</td>
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<td>( D )</td>
<td>Thickness</td>
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<td>Diffusion coefficient</td>
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<td>Pore Diameter</td>
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<td>( D )</td>
<td>Rate of strain (tensor)</td>
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<td>( D_3 )</td>
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<td>( dc )</td>
<td>Concentration gradient</td>
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<td>( \frac{dc}{dx} )</td>
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<tr>
<td>( K )</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>( L )</td>
<td>Fit parameter</td>
</tr>
<tr>
<td>( m )</td>
<td>length</td>
</tr>
<tr>
<td></td>
<td>mass</td>
</tr>
<tr>
<td>Symbol</td>
<td>Meaning</td>
</tr>
<tr>
<td>--------</td>
<td>---------</td>
</tr>
<tr>
<td>$m$</td>
<td>Consistency index</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar Mass</td>
</tr>
<tr>
<td>$\dot{m}$</td>
<td>Mass transfer rate</td>
</tr>
<tr>
<td>$n$</td>
<td>Amount of substance</td>
</tr>
<tr>
<td>$N_0$</td>
<td>Number of activated nuclei under quiescent condition</td>
</tr>
<tr>
<td>$N_f$</td>
<td>Number of flow induced nuclei</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure</td>
</tr>
<tr>
<td>$\dot{p}$</td>
<td>Permeability</td>
</tr>
<tr>
<td>$P$</td>
<td>Power</td>
</tr>
<tr>
<td>$\rho_{\text{pack}}$</td>
<td>Packing pressure</td>
</tr>
<tr>
<td>$q$</td>
<td>Local heat flux (vector)</td>
</tr>
<tr>
<td>$Q$</td>
<td>Heat energy</td>
</tr>
<tr>
<td>$\dot{Q}$</td>
<td>Heat of reaction</td>
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<td>$r$</td>
<td>Ratio between actual and projected surface area</td>
</tr>
<tr>
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<td>Ideal gas constant</td>
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<td>Solubility distance</td>
</tr>
<tr>
<td>$R_C$</td>
<td>Thermal contact resistance</td>
</tr>
<tr>
<td>$R_g$</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>$R_{th}$</td>
<td>Thermal resistance</td>
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<tr>
<td>$S$</td>
<td>Solubility</td>
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<tr>
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<td>Frozen layer thickness</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
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<td>Interfacial temperature</td>
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<td>$T_m$</td>
<td>Material grade specific equilibrium temperature</td>
</tr>
<tr>
<td>$T_{\text{mould}}$</td>
<td>Mould temperature</td>
</tr>
<tr>
<td>$U$</td>
<td>Voltage</td>
</tr>
<tr>
<td>$U^*$</td>
<td>Activation energy of motion</td>
</tr>
<tr>
<td>$U_E$</td>
<td>Internal Energy of Evaporation</td>
</tr>
<tr>
<td>$\dot{V}$</td>
<td>Specific Volume</td>
</tr>
<tr>
<td>$V$</td>
<td>Velocity (vector)</td>
</tr>
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<td>$\dot{V}_{\text{CO}_2, \text{ gaseous}}$</td>
<td>CO$_2$ generation rate</td>
</tr>
<tr>
<td>$V_{\text{H}_2\text{O}}$</td>
<td>Water consumption rate</td>
</tr>
<tr>
<td>$v_i$</td>
<td>Injection speed</td>
</tr>
<tr>
<td>$V_m$</td>
<td>Molar Volume</td>
</tr>
<tr>
<td>$\dot{V}_{\text{MEOH}}$</td>
<td>Methanol consumption rate</td>
</tr>
<tr>
<td>$W_a$</td>
<td>Work of adhesion</td>
</tr>
<tr>
<td>$z$</td>
<td>Valency number</td>
</tr>
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</table>

**Greek**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Thermal diffusivity</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Crystallization</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>charge transfer coefficient</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Fit parameter</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Coefficient of volumetric expansion</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>Fit parameter</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Surface tension</td>
</tr>
<tr>
<td>Symbol</td>
<td>Meaning</td>
</tr>
<tr>
<td>--------</td>
<td>---------</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>shear rate</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>Shear rate (tensor)</td>
</tr>
<tr>
<td>$\delta_D$</td>
<td>Dispersion solubility parameter</td>
</tr>
<tr>
<td>$\delta_H$</td>
<td>Hydrogen solubility parameter</td>
</tr>
<tr>
<td>$\delta_P$</td>
<td>Polar solubility parameter</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Viscosity</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>Zero shear rate viscosity</td>
</tr>
<tr>
<td>$\eta_a$</td>
<td>Viscosity of the amorphous phase</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Contact angle</td>
</tr>
<tr>
<td>$\theta_{app}$</td>
<td>Apparent contact angle</td>
</tr>
<tr>
<td>$\theta_W$</td>
<td>Wenzel angle</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Compressibility</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stress (tensor)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Shear stress</td>
</tr>
<tr>
<td>$\tau^*$</td>
<td>Critical shear stress</td>
</tr>
</tbody>
</table>
1. Background and Objectives

1.1 Introduction to fuel cell systems

The term fuel cell is described by the common definition as “an electrochemical device that converts a supplied fuel into electrical energy (and heat) continuously, so long as reactants are supplied to its electrodes” [1]

This definition shows the difference between fuel cells, classical heat engines and batteries. While heat engines use the heat created in a process, e.g. a combustion, which is transferred via a working substance into mechanical energy (e.g. by a turbine) and then by a generator into electrical energy, fuel cells can convert chemical energy directly into electrical energy [2]. This direct conversion has the advantage that there’s no limit by the Carnot cycle efficiency for fuel cells [3]. This is why fuel cell systems can reach higher theoretical and practical efficiencies than heat engines [4].

Batteries are, just like fuel cells, electrochemical cells based on two electrodes which are separated by an electrolyte. The conversion of chemical energy is based on internal oxidation-reduction reactions for both these systems. The difference between batteries and fuel cells, however, is the way the reactants are provided to the system. For the lifetime of a battery, the amount of chemical energy stored in the system is the limiting factor. Batteries are discharging when in use and have to be reloaded or replaced when the stored energy is used. Fuel cells instead use an external storage device for the supply of the reactants and can therefore run continuously as long as the reactants are supplied. Internal components are not being used during the operation of a fuel cell (besides some wear effects, which reduce the lifetime of a fuel cell system). In a battery, the material of the electrodes is one of the reactants (e.g. primary batteries like: zinc-carbon batteries, alkalimanganese cell or silver oxide batteries) or ions stored in one of the electrodes are depleting at this electrode during operation (e.g. secondary batteries like: lead-acid batteries or lithium-ion batteries). Even though secondary batteries can be recharged by inversing the electrical potential at the electrodes, a continuous operation is not possible [4], [5].

In general four basic parts can be identified, which can be found in a typical fuel cell system [6]:

- Anode: the electrode where the oxidation reaction of one of the reactants takes place
- Cathode: the electrode where the reduction reaction of the second reactant takes place
- Electrolyte: an ion-conductive medium which separates the reactants
- An electrical circuit connecting the two electrodes

Besides these parts, fuel cell systems differ significantly in system volume, system design, used materials, power output, etc. In literature six main classes of fuel cells are typically mentioned[1], [3]. These six fuel cell types are considered viable systems due to their technical maturity or the expected...
potential which comes along with high research activities focused on these fuel cell types [1], [4]. Fuel cells are usually classified by the type of electrolyte used. Several important characteristics for the utilization, such as the operating temperature range, the type of fuel, the types of catalysts, the electrode design and the system design, are mainly determined by the electrolyte. A brief overview of these fuel cell classes can be found in Table 1:

<table>
<thead>
<tr>
<th>Name</th>
<th>Typical electrolyte</th>
<th>Typical Reactants</th>
<th>Operation Temperature Range</th>
<th>Typical Power Output Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline Fuel Cell (AFC)</td>
<td>Potassium Hydroxide (KOH)</td>
<td>Pure Hydrogen (fuel) and Oxygen</td>
<td>50 °C-200 °C</td>
<td>1 kW - 50 kW</td>
</tr>
<tr>
<td>Proton Exchange Membrane Fuel Cell (PEMFC)</td>
<td>Proton conducting Polymer Membrane</td>
<td>Hydrogen and Air or Oxygen</td>
<td>30 °C-100 °C (110 °C-180 °C with modified membrane for high temperature applications)</td>
<td>Up to 300 kW</td>
</tr>
<tr>
<td>Direct Methanol Fuel Cell (DMFC)</td>
<td>Proton conducting Polymer Membrane</td>
<td>Methanol and Air or Oxygen</td>
<td>20 °C-110 °C</td>
<td>Up to 10 kW</td>
</tr>
<tr>
<td>Phosphoric Acid Fuel Cell (PAFC)</td>
<td>Concentrated liquid Phosphoric acid (H₃PO₄) in silicon carbide (SiC)</td>
<td>Hydrogen and Air or Oxygen</td>
<td>~200 °C</td>
<td>50 kW up to 4 MW</td>
</tr>
<tr>
<td>Molten Carbonate Fuel Cell (MCFC)</td>
<td>Mixture of molten carbonate salts (Li₂CO₃, Na₂CO₃, K₂CO₃) in a lithium aluminate (LiAlO₂) matrix</td>
<td>Hydrocarbon fuels (such as Methane) and Air (requires CO₂)</td>
<td>600 °C-700 °C</td>
<td>up to the MW range</td>
</tr>
<tr>
<td>Solid Oxide Fuel Cell (SOFC)</td>
<td>Solid yttria stabilized zirconia</td>
<td>Methane and Air</td>
<td>500 °C-1000 °C</td>
<td>2 kW up to multi MW</td>
</tr>
</tbody>
</table>

The values in these tables are an orientation for the choice of a fuel cell class. Especially the Power Output strongly depends on the system size and the number of single cells combined to a so-called stack. Listing DMFC as its own class in this table is not in agreement with the classification by type of electrolyte, since the same membrane can be used for DMFC and PEMFC. Due to the use of methanol as a fuel, however, these systems differ significantly from PEMFC and are therefore listed separately.

1.1.1 Fuel cell systems and their typical applications

The wide range of operation temperatures (from room temperature up to 1000 °C) and power output (from mW to multi MW) leads to a wide range of possible applications and markets for fuel cell
systems ranging from the power supply of small electronical devices to power and heat supply in so-called combined heat and power (CHP) units for residential blocks. In general, fuel cells could replace their strongest competitors in the long term, namely batteries and heat engines, with several advantages.

**Fuel cell systems vs. heat engines**

Compared to heat engines, fuel cells show reduced environmentally harmful emissions. On the premise that pure hydrogen, which was obtained by electrolysis of water based on renewable energies, is used as fuel, fuel cells offer the potential for zero emission operation. In this case, only water, heat and electricity will be created. For MCFCs and PAFCs running on natural gas, however it was found that the mono Nitrogen oxides (NO\(_x\)) emissions could be reduced by up to 88%, CO emissions by up to 99% and particle matter with a mean aerodynamic diameter of 10 µm (PM\(_{10}\)) could be reduced by 60% compared to combustion based CHP technologies. Another example of efficient emission reduction using fuel cells was found for fuel cells used as auxiliary power units in heavy duty trucks. These units supply electronic devices with energy which are not used for propulsion, such as air conditioning, infotronics, wipers, etc. For these purposes on-board diesel generators are commonly used or the power is drawn from the main propulsion engine. The typical energy range for auxiliary power units spans from less than a kilowatt up to a few hundred kW, which favours the use of PEMFC, but also DMFC and SOFC are being developed for this kind of application. By using a fuel cell system, the emissions could be reduced by: up to 65% for PM\(_{10}\), up to 95% for NO\(_x\) and more than 60% for CO\(_2\), compared to drawing the power from diesel engines [4].

Further advantages of fuel cells compared to heat engines are the direct conversion of chemical energy into electrical energy. In this case, it is not only important that fuel cells do not obey the limit by the Carnot cycle efficiency but also that the number of energy conversions is reduced when the electrical energy is required. Energy conversion is always associated with a reduction in efficiency, unless an ideal, reversible conversion could be achieved. In reality, effects like e.g. frictional heating reduce the amount of energy which can finally be converted into electrical energy by the heat engine system [4].

The efficiency of fuel cell systems does not necessarily scale with the system size. While large heat engines can reach high efficiencies, small fuel cell systems can be as efficient as large ones. For the efficiency of heat engines, smaller systems are critical. With downscaling, the volume to surface ratio is being reduced, which leads to more significant heat losses and the emission legislation is usually more stringent for smaller engines which frequently leads to a trade-off between fuel economy and emissions [4], [8].

On top of that, few to no moving parts can be found in fuel cells. This reduces the tendency to wear. Another plus to the static operation is that fuel cells can operate noiselessly. This is however only half the truth; many fuel cell systems rely on external devices such as pumps and compressors or fans to supply the electrodes with the reactants or fuel reformer for hydrogen generation. Even though these devices are not entirely noiseless, they have a significantly lower noise level than
combustion engines. A disadvantage of these external devices is their power consumption, which reduces the efficiency of the fuel cell system [1], [4].

Several fuel cell systems are currently commercially available where the fuel cell is used in a typical application for heat engines. In the area of stationary micro-CHP (CHP up to 5kW output), various systems are commercially available. For these systems, it has been reported that fuel cell based CHP have globally outsold combustion based ones for the first time in 2012 [9]. Other stationary fuel cell systems find application in emergency back-up power supply and power supply solutions for remote areas like mountains or islands, where a grid extension would be too expensive [4]. Stationary fuel cell systems are the bestseller among the fuel cell systems. Stationary systems account for about 49,000 shipped systems of 71,500 systems shipped in total. Around two third of these systems are installed in Asia. The main part of them is installed in Japan, where the installation of micro CHP units was financially supported by the government under the “ene farm” project. Since this project began in 2009, about 140,000 units have been installed (about 40,000 in 2015). These systems are mainly PEM systems between 0.7 kW and 0.75 kW. The technological improvement, which can be correlated by these kinds of subventions can be seen on the technical specs for a PEMFC CHP system by Panasonic. Between the start of the “ene farm” in 2009 and the 2014 model, the system was reconfigured, simplified and the number of system components was reduced by 15%. The 2014 model uses 20% less Platinum catalyst, its weight was reduced from 90 kg to 77 kg, the durability increased by 10,000 hours to 70,000 h, while the efficiency was kept at 95%. On top of that a blackout function was implemented, which can deliver 500 W constantly for up to 96 h. At the same time, the price for the system was reduced by 50% due to the technical improvement and the production ramp up. The strategy in South Korea differs from the Japanese. In Korea state subventions are mainly granted for fuel cell parks in the multi MW range (usually based on MCFC) [10].

In the area of fuel cell based electrical vehicles, a milestone was reached when Hyundai started mass production of its ix35 fuel cell model [4]. The first cars left the small production line in 2013. This example was followed by Toyota and Honda, releasing fuel cell cars from mass production shortly after (2015 for Toyota and 2016 for Honda) [10]. To be precise these cars, however, have to be considered as hybrid systems since they use a battery for energy storage and breaking energy recovery. An interesting feature of the cars by Toyota and Honda is the possible use as an emergency back-up power supply. Toyota states an output power of 9 kW DC, which can be converted by an add-on AC/DC-converter. Honda is offering room for 5 people and the entire drivetrain fits in the engine compartment [11]–[13]. In the transportation section, a large variety of used fuel cell systems can be found. It ranges from fork lifts over busses to military submarines [4]. In the transport section, sales are dominated by fork lifts but recently deals have been signed, which are about to increase the amount of fuel cell driven systems in mass transit (e.g. trams, buses, etc.). The number of fuel cell busses is still relatively low (83 in Europe, less than 20 in the USA) but about to increase. There is a European subvention program on the way, plans to increase the number of buses in the US (especially in California), and Japan alone is planning to have 100 busses operating for the Olympics in Tokyo in 2020. [10]
Portable power generators are another highly interesting market where fuel cells can replace the commonly used diesel generators. The main applications for these devices are leisure activities such as camping or boating where low power output in the range of a few hundred watts is sufficient. Such systems are offered by e.g. Horizon (Aquigen 180, 180 W max. output), SFC (EFOY-Go, 400 W max. output) and others [14], [15]. Even though these systems have higher capital costs than diesel generators, the operational costs are way lower, and given a sufficient lifetime they might also be more cost effective [16].

**Fuel cell systems vs. batteries**

The main advantages of fuel cell systems compared to batteries can be found in the higher energy density of the fuel and the shorter times for refuelling, which is independent of an electrical grid. These two are mainly competitors in the area of portable devices. In this connection especially the low temperature and low power output systems such as the membrane based DMFC and PEMFC systems are of interest. Diverse prototypes for fuel cell operated consumer electronics (e.g. cell phones, laptops, video-cameras, etc.), lawnmowers and electro bicycles have been presented [8], [17]. Until now, however, very few commercialized systems are available. These are mainly toys such as radio controlled cars, educational packs for schools or grid independent chargers for portable consumer electronics [18].

Predictions from the past concerning the date of market introduction and sales figures of fuel cell systems have often been shown to be over-optimistic due to the large potential of fuel cells [16]. In addition, it was often underestimated how the end-users adapt to changes in technology, the technological development in competing technologies (while that for fuel cell technologies was overrated). A good example of this is the cell-phone. This device was often pointed out as a typical application for a fuel cell powered device with high predicted market shares (exact figures and the according studies can be found in e.g. [19]). These estimations made in the early 2000s were based on the increasing complexity (combined PDA, camera, and cell phone, today known as smartphone) and time of use. Even though these assumptions became true, today’s smartphones are still powered by secondary lithium-ion batteries. While the fuel cell community was claiming that this development would have to be based on fuel cells due to the higher energy consumption, a change in the user’s behaviour (charging every day over-night instead of once a week), the easy access to electrical energy in many countries (even in trains, cars, cafés, etc.), larger battery capacities (3600 mAh for a Samsung Galaxy S7 from 2016 compared to 2100 mAh for the 2012 S3 model) combined with the development of more energy efficient processors resulted in a battery dominated marked, where fuel cells can still be found as prototypes only.

As pointed out by Agnolucci [16] in a rather critical analysis of the market potential of portable fuel cells, buying decisions are based on power density/ specific power, costs, size, energy density and safety. To become a real option compared to batteries, fuel cells have to become at least as user friendly, small, reliable and cheap as batteries. For some niche markets, however, fuel cells can be sold even at a higher capital cost.

It has to be stated, that there are still problems which must be solved to exploit the entire range of advantages of fuel cell systems.
One of the biggest issues is the costs of fuel cell systems. Most of the fuel cell systems are using catalysts based on noble materials such as Platinum, which are cost intensive. The membrane, which is still the one mainly used in membrane based fuel cells, is made of Nafion, a sulphonated tetrafluoroethylene, which is also expensive.

Basically, all the fuel cell systems are suffering from losses which are reducing their efficiency. These losses are due to:

- The overpotential created at the electrodes due to the low reaction rates of the chemical reaction
- Ohmic losses, because of the electrical resistance of the conducting materials
- Fuel crossover, where the fuel crosses the electrolyte without reacting
- Mass transport and concentration losses, when the electrodes cannot be supplied with reactants fast enough to maintain a constant concentration [1].

A more detailed description on the working principle and the problems of a specific fuel cell class can be found in chapter 2.1.

**Problems concerning the hydrogen supply**

For Hydrogen based systems, there are additional problems concerning the production, storage and Hydrogen infrastructure. Hydrogen can be produced by reformation of natural gas obtained from hydrocarbons (e.g. from biomass or fossil sources) or by electrolysis of water. The only way to obtain environmentally friendly hydrogen is through electrolysis, when renewable energy sources such as solar energy, wind energy or water power are used. Even though this is challenging, it also offers the potential to solve problems related to a grid entirely based on renewable energies. These energy sources are not as constant as power plants based on fossil fuels or nuclear power. Therefore, hydrogen could be produced when more energy is available than needed and be used when the energy production is lower than the demand. Controlling this dynamic situation is one of the issues to solve for these so-called smart grids. Today, however, the main source for hydrogen, which is mainly used in the chemical industry, is the fossil type. Most of the fossil sources have a higher energy density than hydrogen and the calorific efficiency of the hydrogen production is not higher than 70%, which is why producing hydrogen as an energy source from fossil sources is a bad solution. Another issue with this hydrogen based solution is the storage of hydrogen. Hydrogen has a high gravimetric energy density, but a low volumetric energy density in gaseous form. It therefore has to be stored under high pressure or in the liquid state at temperatures below -252.9 °C. Another storage solution for large amounts of hydrogen can be found in salt caverns, which are used to store natural gas. For transportation of hydrogen, the same problems as for the storage arise. Hydrogen is mainly transported compressed in tanks, but also pipeline based transportation is possible. There is, however, a lack of infrastructure for a more convenient use of hydrogen as fuel, whether it is for cars or other fuel cell based generators with only 200 (hydrogen-) gas stations expected at the end of 2016 [10], [20].

**Direct methanol fuel cells for the application in hearing aids**

In this work, the focus is on direct methanol fuel cell (DMFC) systems. These systems have several advantages for the use in low power applications, such as the intended use in behind the ear hearing
Hearing aids are a low power application with a restricted system volume. DMFC systems are the system of choice for these requirements. Methanol is a low-cost fuel, which is liquid at room temperature and offers a high volumetric energy density. This enables easy handling and a low storage volume. Another point in favour of DMFC systems for this application is that they can be implemented as passive systems without the need for auxiliary devices (except for a DC-DC converter), which allows for miniaturized systems. On top of that, these systems work at room temperature and can therefore be used close to the body [1], [21].

Conventional hearing aids are powered by tiny button cell batteries. With approximately 50 million people worldwide being equipped with a hearing aid, this leads to the consumption of more than two billion zinc air button cells per year [22]. Changing the batteries produces a huge amount of waste and the battery management can also be an issue for the user [23]. According to estimates by the World Health Organisation (WHO), one-third of the people above 65 years of age are affected by disabling hearing loss (hearing loss greater than 40 dB) [24] and 58% of hearing aid users are older than 70 years. Since manual dexterity deteriorates with age, the battery change becomes increasingly challenging [22]. This problem was solved by Siemens with rechargeable hearing aid batteries. This is, however, directly related to another problem. The recharge time for these batteries is 6 hours, which is a major drawback in case the hearing aid battery goes dead in an inconvenient moment e.g. a business meeting, role play in the theatre, etc. [25]. The use of a DMFC, on the other hand, offers a way faster refuel. The target value for the investigated system is a refuelling time of less than 30 seconds. The refuel process is shown in Figure 1. To simplify the handling the whole hearing aid is used in the refilling process, put in a docking station which contains the fresh methanol. When the button is pushed, the hearing aid is refilled and can be used again.

![Figure 1: Refill process of the DMFC in the hearing aid [22]](image)

The goal is to run the hearing aid with a single refill for 24 h. This calls for a continuous power output of 2.5 mW for 24 h at a voltage above 350 mV with a maximum methanol volume of 200 µl. This goal can only be reached when high concentrations of methanol are used, which is one of the biggest problems in passive DMFC. The project “NanoEnergi”, of which this PhD-project is a part, therefore focuses on different aspects of this miniaturized passive DMFC system [22]:
- Development of new catalysts and new deposition methods for catalyst materials
- Development of new membranes
- Miniaturization of the fuel cell system

This PhD-project was part of the last bullet point. A miniaturized prototype made out of metal was invented at the Danish Technological Institute (one of the project partners). A schematic picture of the system and its single parts can be found in Figure 2. This work deals with the development of a plastic fuel reservoir for this DMFC system.

![Image of fuel cell system](image)

*Figure 2: Schematic of the fuel cell system (LHS) and the single components of the system with a metal fuel container (RHS): Fuel reservoir, gasket, membrane electrode assembly, anode cup, anode current collector and lid including cathode current collector (from left to right)* [22]

### 1.2 Objectives of the PhD-thesis

The overall objective of this PhD-project is to investigate and establish methods for the transfer of the fuel cell container concept into an injection mouldable design, to reduce the costs and production time for the mass production of the fuel cell system.

This can be achieved by the reduction of the process and assembly steps in injection moulding by exploiting in-mould assembly processes to obtain net-shaped or near net-shaped parts. The currently used way of manufacturing the fuel cell container, made out of deep-drawn metal, requires more subsequent manufacturing steps.

The wide range of plastic materials and the resulting variety of available combinations of material properties is another advantage for the injection moulded container: Depending on the final requirements, parts ranging from, for example, inexpensive parts with lower mechanical properties for the use inside a hearing aid casing can be produced while the same equipment and set-up can be used to produce a part made out of a more expensive engineering polymer that could directly be used as part of the hearing aid casing due to its superior mechanical properties. This variability also offers the possibility for fast changes in the properties of the prototype, as long as the part design is not affected.
The specific objectives of this thesis are:

- The design of components for micro injection moulding based on material properties, process characteristics and functional requirements

- The development of the micro injection moulding process with respect to the use of in-process assembly with the aim of reducing the number of assembly and manufacturing operations (e.g. by exploiting in-mould assembly processes like micro insert moulding or micro film insert moulding)

- The development of quality assurance methods for product and process control

- Validation of the functionality of prototypes produced by injection moulding.

To achieve these objectives suitable processes for the realization of the fuel cell container and the functional structure on the inside of an injection moulded container must be found and investigated. An important criterion for the evaluation of these processes is the complexity of the process chain. Therefore, a suitable process with a low number of assembly steps has to be identified.

Based on the process, the design and the application, materials have to be selected and a process window for production has to be found. For the definition of this process window, simulations will be used as well as quality assurance methods. Based on the chosen process these quality assurance methods will have to be developed and applied.

Finally, the functionality of the container will have to be investigated, for example in terms of the methanol retention properties.
2. State of the Art and theoretical background

In this chapter the technical and theoretical background is discussed. Starting with a more in detail discussion of the chosen fuel cell type, this section will continue with a discussion of the production process, namely injection moulding, used in this work.

2.1 Direct Methanol Fuel Cells

There are two main types of DMFC-systems, namely active DMFC and passive DMFC. In an active system, the reactants are supplied to the electrodes using pumps, valves, sensors, etc. for the fuel and fans, compressors, etc. for the supply of oxygen or air. Further components can be used for thermal or water management. In passive DMFC, these issues are dealt with by exploiting phenomena such as gravity, diffusion, fluidic effects such as capillary forces, wetting behaviour and convection. While active systems have the advantage that the supply of the reactants can be controlled and the necessary amount for a certain output can be adjusted, all the auxiliary devices, commonly summarized as “balance of plant”, are increasing the size of the system. Furthermore, some of the auxiliary systems need to be supplied with power which reduces the efficiency of the system. Passive systems, on the other hand, can be designed way more compact and with a simpler structure[1], [26], [27]. The typical structure for the fuel cell part of a single cell passive DMFC-system is shown in Figure 3. It consists of a layered structure of the following components:

- Anode current collector: made of an electrically conducting material (e.g. stainless steel, often coated with noble metals such as gold or platinum for better corrosion resistance and electrical conductivity). Serves as mechanical support for the following layers and as current conducting layer. Furthermore, it has to guarantee the passage of the fuel (methanol and water) to the next layer and allow for the products of the methanol oxidation reaction (MOR, Eq. 2-1) to be removed. The structure implemented in the anode current collector for this purpose is also known as the flow field [27].

- The membrane electrode assembly (MEA): the MEA is the essential part of the fuel cell, where the chemical reactions are occurring. As one can see by the name, it contains both electrodes (anode and cathode) and the proton exchange membrane (PEM):
  - Anode & anode diffusion layer: The anode diffusion layer is in contact with the anode current collector. It usually consists of carbon cloth coated with Polytetrafluoroethylene (PTFE). The hydrophobic properties of this layer enable the venting of the CO₂, which is the product of the MOR. The porous structure of this layer enables a uniform distribution of the fuel over the whole layer. The anode itself consists of the catalyst and an ionomer. A typical catalyst for the anode is a carbon
supported platinum ruthenium (PtRu)-alloy. The ionomer is typically made out of a perfluoro sulfonic acid polymer. The anode is in intimate contact with the membrane. At the anode, a three-phase boundary exists between the catalyst, ionomer and the reactants, at this boundary the MOR occurs. The ionomer enables the proton transport towards the membrane while the electrons are flowing through the carbon structure towards the current collector [27], [28].

- Membrane: This layer is in most cases made out of perfluoro sulfonic acid polymer (Nafion® by DuPont). Nafion® is a material which prevents electrons from crossing but is a good conductor for Protons. The membrane separates anode and cathode electronically and spatially [27], [28].

- Cathode & cathode diffusion layer: This layer has a similar function to the anode layer: Providing the catalyst for the oxygen reduction reaction (ORR, Eq. 2-2) removing the products of this reaction and supplying the catalyst layer with new reactants. The catalyst on this electrode is typically platinum on a carbon structure. And the diffusion layer is often made out of carbon cloth [27], [28].

- Gas diffusion/ water management layer: This layer is an optional layer. Water management can improve the fuel cell’s performance. An additional gas diffusion layer can be used to prevent particles or ambient water to block the porous structure of the cathode diffusion layer [27].

- Cathode current collector: Holds the same function as the anode current collector on the cathode side [27].

- Gasket: Seals the system to avoid fuel evaporation. Isolates the conducting anode structures from the cathode structure electronically.
2.1.1 Working principle of a DMFC

Direct methanol fuel cells (DMFC) are used to generate electricity from an electrochemical reaction where methanol (the fuel) is oxidized at the anode structure according to Eq. 2-1.

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$  \hspace{1cm} \text{Eq. 2-1}

The electrons (e\(^-\) in Figure 3) which are released can be used to power an external electrical circuit (represented by a Resistor in Figure 3), while the protons are transported through the membrane (H\(^+\) in Figure 3). On the cathode side, Oxygen is reduced according to the reaction shown in the following equation:

$$\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$  \hspace{1cm} \text{Eq. 2-2}

This results in the overall reduction-oxidation reaction for the DMFC-system:

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + H_2O$$  \hspace{1cm} \text{Eq. 2-3}
As it can be seen from Eq. 2-1, six electron proton pairs are released per mole methanol, while only one mole carbon dioxide is created. The amount of CO\textsubscript{2} released per generated electron in this reaction is less than for any other saturated alcohol. Methanol is also the only alcohol which can be completely oxidized in PEM systems [26]. These are two of the reasons why methanol is the preferred fuel compared to other alcohols, such as ethanol.

The methanol transport in this passive system is based on gravity that is why the system has to be installed with the fuel cell part at the bottom and the fuel reservoir on top (upside down compared to the schematic in Figure 2 and Figure 3). The fuel then passes through the holes in the anode current collector (see Figure 1) and the anode diffusion layer and reacts at the anode catalyst. The carbon dioxide created in the MOR moves in the opposite direction of the fuel due to buoyancy. On the cathode side, oxygen from the ambient air passes through the diffusion layer and reacts at the cathode catalyst layer. If no water management structure is used, the water created in the ORR is removed by evaporation due to convection.

The passive design has, as already mentioned, the advantage of enabling small systems which leads to a high theoretical energy density, but is at the same time connected to some problems which reduce the systems efficiency.

2.1.2 Effects reducing the efficiency in DMFC systems

Methanol as a fuel offers high theoretical gravimetric and volumetric energy density. On top of that, it can be easily stored in strong plastic tanks which leads to a high storage efficiency and therefore to a high net energy density [1]. A major problem for the commercialization and the use of passive DMFC-systems, however, is the low efficiency. DMFC-systems can in theory reach an output voltage of 1.21 V. This so-called non loss voltage cannot be reached with DMFC-systems in practice due to several effects, which are discussed in the following section[1].

![Image: Theoretical energy densities and specific energies for different fuels and batteries. Abbreviations: L-H\textsubscript{2}: Liquid Hydrogen, CNG: Compressed natural gas. Figure from [3].]
Slow anode reaction rate

The MOR on the anode shows a very low reaction rate. This low activity leads to overpotential at the anode which can be calculated according to the Tafel equation:

\[ \Delta V_{\text{act}} = \frac{RT}{2\alpha F} \ln \left( \frac{i}{i_0} \right) \]

Eq. 2-4

where \( R \) is the gas constant, \( T \) the temperature, \( F \) Faraday’s constant and \( i \) the current density. \( \alpha \) is the charge transfer coefficient which must be in the value range between 0 and 1 and depends on the electrode material and the involved reaction. \( i_0 \) is the exchange current density. At zero current density, the chemical reaction still takes place at the electrode, but the reverse reaction happens at the same rate, at the anode the MOR and its reverse reaction, the reduction of \( \text{CO}_2 \), are in equilibrium. If the electrode surface shows a high activity, this exchange current density is high and the overpotential is reduced. The higher this overpotential the less output voltage can be generated by the fuel cell system. In DMFC-systems overpotentials can be found for both electrodes, but the anode reaction is slower than the cathode reaction [1]. Another issue, especially concerning the anode catalyst is that carbon monoxide can be one of the intermediate products of the MOR [1]. This molecule is poisonous to Pt-catalysts since it adsorbs on the surface and therefore reduces the active catalyst surface. That is why Ru is used in the anode catalyst. Oxygen containing species such as OH-ions adsorb at the Ru, which promotes the oxidation from CO to \( \text{CO}_2 \).

To decrease the overpotential at the electrodes, two main research approaches have been chosen. The first approach is to find a substitute catalyst. Even though several platinum alloys (binary: e.g. PtOs, PtSn, PtW, etc., ternary: Pt-Pd-Ru, Pt-Pd-Co, Pt-Ru-Mo, etc. and quaternary: Pt-Ru-Ir-Sn, Pt-Ru-Ir-Ni) are being investigated, the ideal solution would be a non Pt catalysts, which offers at least the same activity for the MOR, the same durability in the acidic environment of the membrane and a lower price than Pt [1], [28], [29]. To replace the pure Pt catalyst at the cathode three different classes are investigated: heat treated macrocyclic compounds of transition metals, ruthenium based chalcogenides and palladium alloy catalysts. Fewer investigations are published on the replacement of the Pt-Ru catalyst at the anode. Here catalysts based on palladium nickel alloys, osmium based alloys dispersed gold particles on Polyaniline grafted multiwall carbon nano tube matrix and metal free carbon nitride nanotubes have been the topic. All of the platinum free catalysts showed a much lower activity but have the advantage of lower costs and better resistance to poisonous substances [29], [30].

The second approach is based on the preparation of the catalyst. Improving the activity by an increase of the active surface, a homogenous distribution of the catalyst with a controlled particle size and support materials, which allow for a finer dispersion of the catalyst [1], [20], [27]. By improving the structure and distribution of the catalyst, the Pt loadings of the catalyst can be reduced while the reaction rate is unaffected, which is a way to reduce the systems cost [28].

Water and methanol management

As can be seen from the MOR (Eq. 2-1), water is needed at the anode. Therefore it is impossible to run the fuel cell on neat methanol [1]. Diluted methanol solutions as a fuel, however, reduce the
energy density of the fuel cell system. Running the fuel cell on high concentrations of methanol is connected to another problem, the so-called Methanol cross-over. Driven by electro osmotic drag, diffusion and pressure differences between anode and cathode methanol, which has not been oxidized at the anode, can pass the membrane and reach the cathode, where it is oxidized at the Pt-catalysts. This phenomenon has several disadvantages for the fuel cell’s efficiency:

- The methanol which crosses over does not participate in the generation of electricity and therefore, reduces the fuel efficiency
- The oxidation of methanol on the cathode catalyst reduces the availability of the catalyst for the ORR, intermediate products from the methanol oxidation can poison the catalyst and a mixed potential is created at the cathode, which reduces the cathodes potential and therefore the output voltage.
- High methanol crossover can cause membrane degradation which leads to a reduced lifetime of the system [1], [27], [30]

The methanol crossover effect can be reduced using lower methanol concentrations and more effective anode catalysts, both these options are effective ways to reduce the methanol concentration difference across the membrane, which leads to a lower diffusion. The best results for passive systems have been reported for concentrations between 2-4 molar methanol solutions [27] depending on the specific system design. The problem for crossover is that the current state of the art membrane needs to stay hydrated to show proton conductivity. Methanol mixes readily with water and easily diffuses through the hydrophilic sections of the membrane. The approach taken by many research groups is, therefore, based on a modification of the Nafion® material to improve the selectivity between proton conduction and methanol diffusion [1], [27], [28]. This, however, would be only the second best solution, since the material is contributing quite a big share to the overall costs of the fuel cell system and is problematic in respect to its negative environmental impact [22]. Therefore, replacement materials such as sulphonated polyether ether ketone (SPEEK), polyarylene ether sulfone, block co-polymer ion-channel forming materials, etc. have been investigated. SPEEK membranes showed reduced crossover and appropriate conductivity, but the long-term stability of those still remains unproven [27], [30].

Thicker membranes can be used to reduce the crossover, but this will also increase the resistance of the proton conduction. Other approaches to run passive DMFC systems with high methanol concentrations are based on an increase in the mass transport resistance between the fuel container and anode or the use of passive evaporation of the fuel [31]. The use of methanol tolerant catalysts can improve the power output by reducing the mixed potential at the cathode but will not affect the cross-over problems.

On the other hand, water is created at the cathode side and can lead to flooding of the cathode structures when the removal rate by natural convection is lower than the water creation rate in the ORR (Eq. 2-2). Water flooding can lead to cathode structures being blocked by water and therefore to a reduced Oxygen availability which increases the cathode overpotential. When the water removal rate at the cathode is way higher than the creation rate, the membrane can dry out. The membrane has to stay hydrated to be proton conductive. The membrane drying out is typically not a problem for DMFC when operated with diluted methanol. In this case, water cross over from anode to cathode
can occur for the same reasons as the methanol cross over, which increases the risk for cathode flooding. Several approaches including layers for better water removal or pushing the water through the membrane towards the anode have been presented. These approaches are typically based on hydrophobicity/hydrophilicity of the added layers or coatings. Pushing back the water has the advantage that it can be used for the MOR on the anode side and the fuel can, therefore, contain higher concentrations of methanol [1], [27].

Degradation of materials
The fuel cell environment in DMFC is challenging for the selection of the used materials. Methanol is a polar solvent, an acidic section can be found at the membrane, and the electrochemical reactions at the electrodes can be problematic in terms of corrosion, too. The membrane can suffer from mechanical, chemical and thermal degradation during the MEA-assembling and the operation of the system, this can be found as a decrease in conductivity and mechanical strength. In particular in an operation at high current densities the anode catalyst might undergo some changes due to sintering, decomposition, agglomeration of the ruthenium particles and Ru particles, which are crossing over the membrane with water and methanol crossover [27].

CO₂ venting
The effects reducing the fuel cell’s efficiency addressed up to now are only related to the design of the fuel cell, its components and the used materials and are not affected by the fuel cell container design. The carbon dioxide created during the process can have a negative influence on the fuel cell’s efficiency. The CO₂ increases the fluidic resistance for the methanol passing the anode diffusion layer and can block the anode flow field. Furthermore, it can lead to a pressure build-up in the container which leads to a higher pressure-difference between anode and cathode and therefore to an increase in the cross-over problematic. Venting the CO₂ from the container without losing fuel is therefore important for the efficiency [26].

Several research groups have been working on this topic with a large variety of approaches:

Ye and Zhao [32] used a fuel feed and CO₂ removal system based on gravity. The fuel tank was on a higher level than the fuel cell which leads to a hydrostatic pressure driven flow through a vertically mounted serpentine flow field. The emerging CO₂-bubbles reduce the density of the liquid which is then driven by the pressure gradient pushed back in the fuel container from where the CO₂ is released through a vent valve.

Chan et al. [33] proposed a pressure controlled passive valve to release the CO₂. This valve also operated a valve for the fuel supply which led to a self-regulated fuel feed rate to minimize the fuel crossover.

Paust et al. [34] used tapered channels in the anode flow field to create a capillary pumping mechanism. The CO₂-bubbles move along the hydrophilic channels due to different curvatures at the bubble surface caused by the increase of the channel diameter in the flow direction. This leads to a pumping mechanism which can be used to drag fresh fuel into the end of the flow field with the smaller channel cross-sections and vent the CO₂ at the other end of the flow field. The same mechanism was used by Sun et al. [35].
Prakash and Kohl [36] investigated PTMSP/1,6-divinylperfluorohexan membranes and found that they are promising candidates for CO₂-venting applications in DMFC since they showed a high selectivity between CO₂ and methanol and venting efficiencies of up to 80%.

Meng and Kim [37] showed a fuel supply system based on a spring loaded fuel container bottom to generate the pressure which was driving the CO₂ through hydrophilic channels to a venting spot based on a hydrophobic porous membrane. To avoid movement of the bubbles away from the venting spot, they used virtual check valves (a narrow cross-section in the flow channel).

In this work, the approach described in [38] was followed. The venting in this case is based on a hydrophobic porous material (with interconnected pores) on the walls of the fuel container shown in Figure 2 in proximity to the anode current collector. For the investigated system, the current collector is not using a flow field design to transport the fuel in parallel to the surface of the anode diffusion layer but rather circular holes to create a flow perpendicular to the anode diffusion layer supplying the anode with methanol based on gravity and capillary forces. The CO₂ has to leave the diffusion layer through the same holes. Due to the hydrophobicity of the surface the CO₂ is attracted to the surface of the porous material and can be vented through the pores and venting holes on the outside wall of the container.

2.2 Injection moulding

Injection moulding is one of the key production methods in plastic processing. Nowadays more than one-third of all thermoplastic materials are processed by injection moulding. This process enables the production of net-shape or near net-shape parts with a complex geometry in a cost-efficient production for medium to large part numbers. Short cycle times and the parallel replication of several parts in multi-cavity moulds with precise dimensions and a high reproducibility make this process ideally suited for mass production of thermoplastic parts [39], [40].

In addition, injection moulding is an extremely versatile process. Parts in the weight range from a few milligrams up to several kilograms can be produced. Although thermoplastic materials are the main application for injection moulding, other polymeric materials such as thermosetting plastics and elastomers can be used.

When ceramic or metallic powders are mixed into a thermoplastic material matrix, it is even possible to produce metallic or ceramic green parts by injection moulding. These parts, however, have to be sintered to obtain the final shape, size and mechanical properties [41]–[43].

In the following section the injection moulding process is explained based on the process for thermoplastic materials.

Figure 5 shows a schematic of the parts directly involved in the injection moulding cycle. A process cycle begins with the injection of a well-defined amount of molten polymer into the cavity between the fixed and the movable mould half of the closed mould (see Figure 6: Injection). The injection in a conventional injection moulding machine is done by a lateral translation of the screw towards the nozzle. A check valve at the tip of the screw prevents backflow of the material.
Once the specified amount of material is injected, a holding pressure is maintained which pushes more material into the cavity to compensate for the shrinkage of the part during solidification. This packing phase is effective until the gate\footnote{The gate is usually the thinnest cross-section of the part. It is the section where the part is separated from the channel structures used to distribute and supply the liquid material to the cavity such as runner and sprue.} is solidified and the material supply to the cavity is stopped (see Figure 6: Packing).

The packing phase is followed by the cooling phase, where the part solidifies further. To speed up the cooling process by interrupting the heat flow from the hot nozzle to the chilled mould, the barrel can be moved away from the mould during the cooling phase (as long as a nozzle valve is used). To save cycle time, the material for the new shot is metered during the cooling phase. The raw material is stored in the hopper, usually in granulated form, from where it falls into the barrel. The rotating screw moves the material towards the tip. At the same time, the material is heated by frictional forces due to the screw rotation and the heat from the heating bands. The heat introduced into the material leads to the plastification of the thermoplastic material. The screw rotation additionally leads to a homogenization of the melt. The plasticated material accumulates in front of the screw since the check valve enables the flow in that direction. The pressure created in front of the screw pushes the screw back until the specified volume of melt for the next shot is reached in front of the screw (see Figure 6: Cooling and plasticating).
Typically, the cooling time is the largest share of the total cycle time, and depends on cooling conditions such as the temperature difference between the melt and the mould and the wall thickness.
of the part. Once a large enough portion of the part is solidified to provide sufficient mechanical stability, the mould is opened and the part is ejected by an ejection system (see Figure 6: Ejection).

After the part is ejected, the ejection-system is pulled back in its zero position and the mould is closed. If the barrel was moved, the nozzle is brought back into close contact with the mould and the injection moulding cycle is started again [42].

### 2.2.1 Special moulding processes

Earlier in this chapter, the versatility of the injection moulding process regarding the materials which can be used was already mentioned. This, however, is not the entire range of possibilities offered by the injection moulding process.

Over time, several processes have been derived from the conventional injection moulding process and are presented here briefly:

**Injection compression moulding**

In injection compression moulding, the melt is injected into a cavity with an enlarged cross-section. This eases the filling of sections with a narrow-cross-section in the final part and results in lower injection pressures. A closing movement of the mould is then used to fill and pack all the structures in the cavity. Compared to the packing phase in conventional injection moulding, the compression leads to a more uniform pressure distribution across the cavity and therefore to more homogenous physical properties, less shrinkage, warpage and lower moulded-in stresses.

**Lost core moulding**

Lost core moulding is based on a soluble or fusible core structure. This core is overmoulded and removed from the solidified part afterwards. This technique enables complex structures inside an injection moulded part such as undercuts.

**Co-injection moulding**

This process, also known as sandwich moulding, can be used to exploit the optimal properties of different materials in one part. Two materials can be injected sequentially or concurrently, one of the materials forms the core of the part while the other forms the skin layer. Therefore, it can be used to create stiff parts with a soft surface, for example.

**Fluid assisted injection moulding**

In principal, the process is similar to Co-injection moulding besides that, instead of a second material, a gas or a liquid are injected to form the core structure. This process can be employed to create hollow injection moulded structures.

**2K-moulding**

Similar to Co-injection moulding, the 2K-approach is used to combine different materials. In this case, however, the first material is used to mould a part which is overmoulded by a second part made out of the second material. This can be done by using the first moulding as an insert in another mould (cavity transfer process), which is a suitable approach for a conventional injection moulding
machines. In specialized 2K-injection moulding machines, a second barrel containing the material for the second shot is used for the sequential moulding operation. The cavity for the second component can be provided by different approaches, e.g. by mounting the movable mould half on a rotating disc or by the core pull technique. In the first approach, the movable mould half is rotated to the position of a second cavity where the overmoulding is happening. In the second approach, a core is used to separate the first shot cavity from the second shot cavity. After the first shot, this core is pulled out to open the flow channel to the second cavity. Like the Co-injection process, 2K-moulding can be used to create, e.g. soft features on a part made out of hard plastics, two coloured parts, or sealing structures made out of thermoplastic elastomers on parts made out of other thermoplastics.

**Structural foam injection moulding**

This technique is used to create parts with a solid skin layer and a foamed core layer. Physical or chemical blowing agents are dissolved in the melt (gases like nitrogen as physical blowing agent) or mixed into the pellets (chemical blowing agents), and this mixture is injected in a pressurized cavity. The amount of material injected is a short shot which means that the cavity is not entirely filled. After injection, the cavity pressure is released and the gas from the blowing agents expands. The gas expansion pushes the plastic to fill the cavity and produces voids in the core of the part.

A similar approach is used in the so-called MuCell® process, also known as Microcellular moulding. This process uses supercritical gases (such as nitrogen or carbon dioxide) mixed into the polymer melt to create highly uniform microscale cells in the range of 0.1 to 10 µm.

By utilizing this process the amount of plastic and therefore the part-weight can be reduced, while part toughness, fatigue life and impact strength can be increased.

**Insert moulding**

Insert moulding is a very efficient process to increase the functionality of injection moulded parts. In insert moulding, inserts made out of any material which is compatible to the injection moulding process (in terms of temperatures, pressures, shear stresses, etc.) can be used. Therefore, parts with even contradictory properties can be created, e.g. by overmolding of a metal insert an electrically conducting part with an isolating shell. This process can reduce the assembly steps in production and therefore reduce the production costs for multi-material components. Based on the role of the insert, three different techniques can be distinguished for insert moulding:

- **Insert-technique**: here the main mechanical structure is made out of the injection moulded material and the moulded material has the largest share in mass and volume. The inserts are functional elements added to the plastic part such as metal thread inserts.
- **Outsert-technique**: the outsert-technique is the opposite of the insert-technique. Here the main structure is represented by the insert while the moulded parts add functionality such as snap fit joints.
- **Hybrid-technique**: this technique exploits specifically the different physical properties of the used materials such as mechanical strength, electrical conductivity, chemical resistance, etc.
A further process based on insert moulding is film insert moulding (FIM), also known as in-mould labelling or in-mould decoration. In this case, the insert is a preformed film. This technique is often used to improve the surface finish of plastic parts or their optical and haptic appearance, but can also be used to increase the functionality of the part. [44]– [47]

2.2.2 Micro injection moulding

Micro injection moulding (µIM) is, besides hot embossing, considered the potentially most viable process for the production of thermoplastic micro parts [48]. The main areas of interest, which can typically be found in literature, describe the micro injection moulding process typically based on properties of the produced parts, which are [49]:

- Parts with a mass in the range of micrograms to a few milligrams
- Parts with structures or details in the micrometre range
- Parts with larger dimensions but tolerances in the micrometre range

µIM became of interest in the late 1980s when micro parts were moulded on modified conventional machines [50]. This approach, however, is problematic for several reasons for the production of micro parts. The first reason is the low shot-weight. Applying a conventional machine to produce parts in the sub milligram range leads to a large amount of waste material due to the over-dimensioned sprue and runner system. This is also a problem concerning the cycle time, since it is not determined by the cooling time necessary to cool the part but rather the cooling time of the sprue [51]. Along with the extended cycle time and the small amount of melt injected comes the problem of a long dwelling time of the material in the barrel, which can lead to thermal degradation.

Due to the size of the standard pellets, the screw size of conventional injection moulding machines reaches a minimum limit of around 12 mm in diameter, so that the pellets can still be plasticated and the screw still has enough mechanical stability to withstand the injection pressures [48]. These screw diameters are problematic for the metering and injection accuracy since one millimetre travel of the screw can correspond to an injection of 200 times the part-weight [51]. In small cross-sections, particularly high cooling rates can be found due to the high surface to volume ratio. One way to fill these sections is to use high injection speeds. In a conventional machine, rather large masses have to be moved, which results in limited acceleration due to the inertia of the system. This strongly affects the moulding process, where high injection speeds over short injection distances are required. This represents another issue in the use of conventional machines [49]. For these and other reasons, machines have been developed which are specialized for the needs in micro injection moulding.

Most of these machines are based on the separation of the plastification and the injection process and a downscaling of the machine and its functional parts. For the plastification, screws with a diameter below 20 mm in a heated barrel are typically employed. These screws are driven by a servo electric actuator, which provides a high level of accuracy. The small screws do not have to withstand the injection pressure but only the back pressure during the metering which is typically much lower. Therefore, smaller screws can be used for the plastification of standard pellets. A second possibility
for plastification can be found in the use of a plunger in combination with a hot cylinder (see Figure 7) [48], [49].

An entirely different plastification principle can be found in a recently commercialized µIM-machine [52]. In this system, a sonotrode is used for the plastification of the pellets by introducing the necessary energy by ultrasound.

In most of the µIM machines, the melt is then transferred into an injection cylinder and injected into the cavity. A plunger is typically employed for the injection. The diameters are typically in the range of 2 to 7 mm [51], [53].

Another approach is taken by Arburg with their micro injection unit. This unit can be mounted on a conventional injection moulding machine. A screw with a diameter of 15 mm or 18 mm is used for pre-plastification and a small screw of only 8 mm is used for metering and injection [54].

Apart from the plastification, metering and injection issues, µIM can require special processing conditions. Since structures of the part can be in the scale of the venting structures in conventional moulding, trapped air can become problematic. Air in the mould can lead to structures not being filled entirely or, especially at high injection velocities, to burned material when the air is compressed and heated up quickly (also known as the “diesel effect”). A sufficient venting rate is therefore important in µIM. Otherwise, a vacuum pump can be used to evacuate the mould before the injection. This, however, can reduce the mould-surface temperature and therefore deteriorate the replication of microstructures when temperature sensitive polymers are used [55].

Another issue in µIM is the control of the mould temperature. Especially for the filling of micro structures with high aspect ratios, it might be necessary to keep the mould temperature close to the melt or glass transition temperature (for crystalline and amorphous materials respectively) during the
injection phase [48]. After the part is filled, the mould temperature has to drop below the ejection temperature to provide sufficient cooling. This so-called variotherm process extends the cycle time compared to conventional moulding with a fixed mould temperature, but has the advantage of avoiding short shots and weldline creation and reduced internal stresses [48].

To create moulds for µIM, the machines used in conventional tooling approaches are usually not precise enough. Therefore, processes like laser ablation, refined conventional processes such as micro-milling and micro electro discharge machining or processes originally developed for the semiconductor or micro electro mechanical systems (MEMS) production, like deep reactive ion etching (DRIE), LIGA (German acronym for: lithography, electroplating and moulding) and micro stereo lithography can be applied to create micro-structured surfaces and moulds for parts with micrometre dimensions [49].

Micro structures in the shape of V-grooves, ribs, pillar and cone arrays have been successfully produced by µIM with lateral dimensions between less than 0.1 µm and 100 µm with aspect ratios up to 4 [56], [57].

2.2.3 Film insert moulding

The FIM process has already briefly been described in section 2.2.1. This process was chosen for the implementation of the fuel cell container based on the process selection, which is presented in section 3.1. Therefore, a more detailed review of the state of the art in this process is given in this section.

In Film Insert Moulding, a preformed film is inserted in the mould and subsequently overmoulded. This injection moulding technique is mainly used to create decorative plastic parts with a high-quality surface finish. These parts are, for example, used in the automotive industry as well as for mobile phones and many other applications [58]. Apart from this, FIM has been used to add functional features like nano-patterned structures [59] or radio frequency identification tags (RFID-tags) [60] to the surface of injection moulded parts. Furthermore, the use of FIM to overcome the mechanical problems of weld lines in glass fibre filled thermoplastics has been reported [61]. Despite its manifold applications, the number of scientific publications on the topic is quite low.

One of the key areas of research on FIM is the effect of the change in the cooling rate of the part when a film is inserted. A plastic film insert decreases the heat conduction between the melt and the mould, which influences the filling and cooling behaviour of the part. The warpage resulting from these uneven cooling conditions was investigated in several publications [58], [62]–[64].

Chen et al. [64] reported an asymmetric flow behaviour of Polypropylene when a film was inserted, where the mould side covered by the film showed a flow leading effect. Furthermore, they proposed a parameter called “Retardation-induced temperature drop (RTD)”, which describes the delay they found for the mould surface covered by the film insert to reach the maximum temperature. While this happens almost simultaneously in conventional injection moulding in their mould, the film covered side was heated up slower by the melt in FIM. They found that warpage increases with an increase in RTD. RTD itself was found to increase with an increase in film thickness, with an increase in melt temperature at constant mould temperature and to decrease with an increase in mould temperature.
at a constant melt temperature. These results are in good agreement with the reduced heat flow rate on the mould side with the film due to the additional thermal resistance of the film and the thermal contact resistance of the film mould interface compared to the uncovered mould side [65]. This effect also leads to the increase in asymmetry of the Temperature distribution with an increase in the thickness of the film insert found by Kim, et al.[66].

Kim et al. [63] found a phenomenon they called “Warpage Removal Phenomena (WRP)” in FIM Parts made out of a PC/ABS blend and a laminated film (0.45 mm thick ABS layer and 0.05 mm PMMA). This WRP describes the fact that the direction of warpage changed from a convex shaped film side of the part to a concave shape, when the parts where annealed after moulding and the film has not been annealed before being inserted into the mould. When the film was annealed before moulding, this phenomenon did not occur. They concluded that the reason for WRP is the thermal shrinkage of the unannealed film during annealing due to the relaxation of residual stresses in the film from film production, which leads to a negative coefficient of thermal expansion (CTE) for the unannealed film.

Another area of interest in FIM-research deals with the interface between the film insert and the injection moulded substrate. Hereby, especially the adhesion between film and substrate and the morphology at the interface were investigated. As described a bit more in detail in [67], the adhesion strength between two polymers can be influenced by different underlying mechanisms such as:

- A large interface area, which allows for a high number of molecular binding interactions or mechanical interlocking between the materials (e.g. a rough surface)
- Wetting behaviour between the Polymers
- Inter-diffusion and entanglement of polymer chains at the Interface, when the interfacial temperature is high enough

Leong, et al. [68] stated that the bonding strength between a PP film and a PP substrate can mainly be improved by increasing the injection speed and the packing pressure. Even though an increase in bonding strength can be observed with increasing interfacial temperature, the improvement in bonding strength due to a higher barrel temperature is limited. Increasing the barrel temperature above this limit only has negligible effects on the interfacial temperature. Furthermore, they suspect an increase in crystallinity in Polypropylene, which they used as a substrate due to the slower cooling under the film contributing to a reduction of the toughness of the FIM-part.

Investigating the morphology of FIM-parts made out of polybutylene terephthalate (PBT) and a laminated ABS/PMMA-film, Kim, et al. [69] found the highest distribution of amorphous domains in the bottom of the FIM-part, which was facing the uncovered mould using FTIR images, which can be explained by the formation of an amorphous skin layer where the melt is quenched at the mould wall and the cooling rate is higher than the crystallization rate. On the other side of the part, they found a lower distribution of amorphous domains, which indicates a lower cooling rate and therefore a higher amount of crystallization while the distribution of amorphous domain was lowest in the core region, which has the lowest cooling rate. These findings were confirmed by WAXD profiles and DSC scans. While both of these methods showed that the highest crystallinity was found in the core region of the part, the WAXD-profiles showed slightly larger crystals in the bottom than in the top of the
FIM-part. This was explained by the transparency of the amorphous layer for x-rays, which results in a measurement of the layer right above the amorphous skin layer. In the DSC scans, they found almost no difference between the top and the bottom because of the very thin skin layer.

Chen, et al. [64] showed that the crystallinity of the substrate and the size of the crystallites increases with a decrease in the cooling rate due to the film insert. This also leads to an increase in warpage of the part.

In contradiction to the increase of adhesion with increasing injection speed, which was found in [68], Leong, et al. found lower peel strength for the combination of a PET-Film and a PET-substrate at an injection speed as high as 500 mm/s compared to the low level of 50 mm/s [70]. This was explained by the increase in molecular orientation due to the higher shear rates at higher injection speeds. A high molecular orientation provides shorter, free molecule chains, which can diffuse through the film substrate interface and create molecule chain entanglements, which are important for good adhesion. In highly oriented regions, it is expected that only short side branches entangle, which show weak anchorage and therefore bad interfacial bonding. Annealing of these FIM-parts deteriorated the peel-strength even more. It is assumed that the crystallization which occurs during annealing reduces the number of loose molecules that are available for entanglements when the molecule chains realign and fold to form the semi crystalline structure. This is in good accordance to the lower peel strength, which was found for higher crystallinity. Longer annealing times led up to a certain point to an increase in crystallinity and therefore to a decrease in peel strength until both values became constant. In accordance to [68], a higher barrel temperature was found to result in a higher film substrate peel strength. The apparent contradiction, which was described in the beginning of this paragraph can be explained by the investigated injection speed ranges. While the investigated injection speeds in [68] are quite low and in a narrow range (10, 40 and 70 mm/s), the difference between the high and the low level of injection speed in [70] are 50 and 500 mm/s. Therefore, it is expected that the effect seen in [68] is based on the decrease in viscosity and a better adhesion due to a closer contact between the molten polymer and the film insert while the dominating effect in [70] is the orientation of the molecules due to the high shear rates, which reduces the adhesion. A direct comparison of these findings however is not possible since different machines and moulds were used. The screw diameter is not mentioned in the publications and therefore the actual flow rate is unknown.

Martinez et al. [71] investigated the overmoulding of fabric. They stated that the pressure drop between two points in a mould for a spiral shape part was 12-15% higher when an upholstery fabric was inserted into the mould. The investigated fabrics consisted of a sandwich structure with a fabric layer, a foam layer and a “protective liner”, where the last-named layer was overmoulded. Since the pressure drop was mainly influenced by the thickness of the foam layer, they related the pressure drop to the compression of the foam layer.

**Film insert moulding – Literature review summary**

Warpage in FIM is found to be related to asymmetrical cooling conditions of the melt due to the thermal resistance of the film insert. This thermal resistance leads to a reduced heat flow rate towards the film covered surface. The presented RTD-value is a reciprocal measure for the heat flow
rate through the film insert. For a precise prediction of the warpage effect, it is necessary to consider more than just the thermal condition. Residual stresses in the film insert, for example, can have a large influence, as shown by the warpage removal phenomenon when FIM-parts are annealed. Other influences can be found in e.g. the ratio between the film and the overmoulded part thickness and the packing conditions.

The adhesion in film insert moulding was found to depend on the injection speed, the packing pressure and the interfacial temperature between the film insert and the melt. While an increase in packing pressure results in better adhesion, the increase in adhesion due to an increasing barrel temperature was found to have a limited effect above a certain temperature. The injection speed was found to increase the adhesion when increased in small steps at a lower level, while for too high injection speeds the orientation of the polymer chains reduces the adhesion. For semi-crystalline materials, a higher crystallinity was reported under the film insert than on the uncovered interface due to the lower cooling rate caused by the film insert. An increase in crystallinity reduces the adhesion and can cause warpage.

### 2.3 Injection Moulding Simulations

Injection Moulding is a process, where many complex interactions can be found, e.g. between the parameters which can be set on the machine (like for example the barrel temperature, the injection speed, etc.), the resulting material behaviour and finally the resulting product [72]. The complexity of the process and the differential equations, which are used for the mathematical description of it makes it impossible to accurately predict the outcome by analytical means, and therefore favours the use of computer based numerical simulations to avoid time and cost intensive experiments and mould redesign whenever possible. Therefore, injection moulding simulations can be considered to “bridge the gap between research data (i.e. the behaviour expected) and the behaviour in practice”[73].

For solving the mathematical model for the injection moulding process, which is based on a set of governing equations, models for the material behaviour and the associated boundary conditions [72], a Computer Aided Design (CAD) model is created and subsequently divided into small elements to create a mesh, which is a representation of the geometry of the CAD model consisting of a large number of elements with a simple geometry. Eventually, the equations of the mathematical model can be solved at discrete time steps for the nodes at each corner of an element. The obtained values are then used as boundary conditions for the calculation of the moulding properties of the adjacent element. This so-called Finite Element Analysis (FEA) is well suited to solve the governing equations, even for complex parts [72]. The computation time of a simulation mainly depends on the number of elements chosen for the representation of the model and the number of time steps. The trade-off for every simulation is, therefore, between the computation time and the time and the spatial resolution of the simulation result.
2.3.1 Governing equations

Under the assumption that the fluid is a continuum, which means that its molecular structure is ignored and the physical properties can be defined at a point in the fluid and vary only smoothly over space and time so that differentiation is permissible, the governing equations for the calculation of the moulding properties are:

- The conservation of mass:

\[
\frac{D\rho}{Dt} = -\rho \nabla \cdot \mathbf{v} \tag{Eq. 2-5}
\]

- The conservation of momentum:

\[
\rho \frac{D\mathbf{v}}{Dt} = \rho \mathbf{g} + \nabla \sigma \tag{Eq. 2-6}
\]

- And the conservation of Energy (in terms of temperature):

\[
\rho c_p \left( \frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right) = \beta T \left( \frac{\partial p}{\partial t} + \mathbf{v} \cdot \nabla p \right) + p \mathbf{v} \cdot \mathbf{v} + \sigma : \mathbf{\nabla v} + \nabla \cdot (k \nabla T) + \dot{Q} \tag{Eq. 2-7}
\]

The explanation for the symbols in these equations is shown in Table 2.
Table 2: Symbols used in governing equations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Additional explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{D}{Dt}$</td>
<td>Material derivative</td>
<td>Takes the motion of a fluid particle along a stream path and its changing value over time into account</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td></td>
</tr>
<tr>
<td>$\rho$</td>
<td>Fluid density</td>
<td>As a function of position and time $\rho = \rho(x,y,z,t)$</td>
</tr>
<tr>
<td>$v$</td>
<td>Velocity</td>
<td>At a point in the fluid $v = (x,y,z)$</td>
</tr>
<tr>
<td>$g$</td>
<td>Total body force per unit mass</td>
<td>Only considering body forces due to gravity. Further possible body forces could be e.g. centrifugal and electrostatic forces, which usually don’t have to be considered in Injection moulding</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stress tensor</td>
<td></td>
</tr>
<tr>
<td>$c_p$</td>
<td>Specific heat capacity</td>
<td>Measured at constant pressure</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>Coefficient of volume expansion</td>
<td>$\beta = \frac{1}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial T} \right)_p$, where $\bar{V}$ is the specific volume</td>
</tr>
<tr>
<td>$k$</td>
<td>Thermal conductivity</td>
<td></td>
</tr>
<tr>
<td>$\dot{Q}$</td>
<td>Heat of reaction</td>
<td>Usually ignored for injection moulding simulations of thermoplastic polymers</td>
</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
<td></td>
</tr>
</tbody>
</table>

In Eq. 2-7 $\nabla v$ is the scalar product of tensors defined as:

$$A:B = A_{ij}B_{ij}$$ \textit{Eq. 2-8}

Where $A$ and $B$ are tensors [72].

2.3.2 Modelling of material properties

To use the governing equations to simulate the injection moulding process, further information on the material behaviour is needed. Polymer materials show viscoelastic properties, which means that plastic shows the “tendency (…) to respond to stress (or strain) as if it were a combination of an elastic solid and a viscous liquid. (…) As a result, the response to stress depends on both the rate of the stress and the time for which it is maintained” [74]. This behaviour influences and is exploited in the injection moulding process. Therefore, a row of mathematical models exists of which the ones commonly used in Injection moulding simulation software are presented in the following section.
**Viscosity**

Viscosity ($\eta$) is defined as the ratio of the shear stress ($\tau$) and the rate of shear deformation ($\dot{\gamma}$):

$$\eta = \frac{\tau}{\dot{\gamma}}$$  \hspace{1cm} \text{Eq. 2.9}

and is a measure for the fluids inner resistance to flow processes [75]. Where $\tau$ and $\dot{\gamma}$ are tensors. For so-called Newtonian fluids, the viscosity is constant as long as the temperature is constant.

Polymer melts, however, display a shear thinning behaviour and are, therefore, considered as non-Newtonian fluids. This shear thinning behaviour is expressed by a decrease in viscosity with an increasing shear rate. This effect can be observed in Polymers beyond a critical shear rate ($\tau^*$). Below that shear rate, the viscosity is almost constant, similar to that of Newtonian fluids. A typical double logarithmic plot for viscosity over shear rate can be found in Figure 8.

![Figure 8: Plot for the shear rate dependency of the viscosity. Red line: Newtonian plateau, Blue line: Power-law region, Black line: Cross-WLF model](image)

Different models to describe this behaviour have been presented in the past. The most commonly used models are the power law model, the Carreau model and the Cross model.

The power law model has the form:

$$\eta(\dot{\gamma}) = m\dot{\gamma}^{n-1}$$  \hspace{1cm} \text{Eq. 2.10}
where \( m \) and \( n \) are material constants. They can be found from the linearly decreasing power law section in the \( \log(\eta) \) vs. \( \log(\dot{\gamma}) \) plot in Figure 8. This model can easily be fitted to experimental data obtained at high shear rates, but ignores the Newtonian-behaviour of polymer melts at lower shear rates. During the injection moulding process, both high and low shear rates can be found. High shear rates usually occur during the injection speed controlled filling phase, while the packing phase is governed by low shear rates when the flow rate is determined by the shrinkage of the material. Therefore, the power law model is insufficient to model the viscosity during the entire process [72].

Both the Carreau and the Cross model are considering the Newtonian region. Since the Cross model was found to fit the shear rate data better, it is commonly used in commercial simulation software and therefore presented here.

\[
\eta = \frac{\eta_0}{1 + \left( \frac{\eta_0 \dot{\gamma}}{\tau^*} \right)^{1-n}} \tag{Eq. 2-11}
\]

In this equation, \( \eta_0 \) denotes the zero-shear-rate viscosity, \( \tau^* \) is a constant related to the shear rate at the transition from the Newtonian to the power law behaviour and \( n \) is the power law index.

The temperature dependence of viscosity was already mentioned for Newtonian fluids, but is true for polymer melts, too. The viscosity of polymer melts decreases with increasing temperature. This effect is usually accounted for by the concept of time-temperature superposition. This concept allows calculating the unknown viscosity at a temperature \( T \) by shifting the known viscosity at a reference temperature \( T_0 \) along the logarithmic time axis by the amount \( \log \left( \alpha_T(T) \right) \). An empirical model based on this concept can be used to implement the temperature dependency in the Cross model, which leads to the Cross-WLF (Williams-Landel-Ferry) by using the time-temperature superposition on \( \eta_0 \):

\[
\eta_0(T) = D_1 \exp \left( \frac{-A_1(T - D_2 - D_3P)}{A_2 + T - D_2} \right) \tag{Eq. 2-12}
\]

where \( D_1, D_2, D_3, A_1, \) and \( A_2 \) are constants. In Eq. 2-12, \( D_2 = T_0 \) and \( D_3 \) is the influence of pressure on viscosity. In most injection moulding simulations, \( D_3 \) is set to zero, even though the influence of this parameter is quite relevant due to the high pressure levels in injection moulding, especially during the filling phase [75], [76].

In the governing equations (section 2.3.1), viscosity plays an important role for the stress tensor \( \sigma \) of a so-called generalized Newtonian fluid which is defined as:

\[
\sigma = -pI + 2\eta D \tag{Eq. 2-13}
\]
Where \( \mathbf{I} \) is the identity matrix and \( \mathbf{D} \) the rate of strain tensor, given as:

\[
\mathbf{D} = \frac{1}{2} (\nabla \mathbf{v} + (\nabla \mathbf{v})^T)
\]  

Eq. 2-14

where the superscripted \( T \) indicates the transpose operation of the matrix. This stress model considers non-Newtonian behaviour but ignores the influence of viscoelastic effects like memory or elasticity (e.g. recoil, stress relaxation and extrudate swell) [75] and is therefore mainly useful for shear force dominated flow processes [72].

**Specific heat capacity and thermal conductivity**

The specific heat capacity indicates how much energy is needed to raise the temperature of a unit mass of material by 1 °C. It can be measured at isobaric or isochoric conditions where the use of the isobaric measurement is more common [72], [75] and is given as [77]:

\[
c_p = \frac{Q}{m \Delta T}
\]  

Eq. 2-15

In injection moulding simulations, this parameter is important for the calculation of the heat transfer between the melt and the mould. In the range of processing temperatures, the specific heat capacity varies only modestly but it shows a discontinuity for semi crystalline materials due to the latent heat at crystallization [72], [75].

The thermal conductivity \( (k) \) is a measure for how good heat is conducted through a material. For simulations, the thermal conductivity of both, the melt and the mould is needed. Polymers show a way lower thermal conductivity than Metals. The thermal conductivity can be found by:

\[
\frac{dQ}{dt} = -k A \frac{dT}{dx}
\]  

Eq. 2-16

respectively by dividing Eq. 2-16 by \( A \) and generalizing the derivative as:

\[
\mathbf{q} = -k \nabla T
\]  

Eq. 2-17

where \( Q \) is the amount of heat transferred, \( A \) the area through which the heat flux occurs, \( t \) the time and \( T \) the temperature. \( \mathbf{q} \) is the local heat flux vector. Eq. 2-17 is the so-called Fourier’s law, where \( k \) is a scalar, which can vary with pressure and temperature. For polymers, this relation has to be modelled more complexly. They do not only show a dependency on temperature and the phase the polymer is in (solid or liquid), which is different for amorphous and semi crystalline materials [75], but also on pressure, molecular orientation (due to the high shear rates in injection moulding) and for semi-crystalline materials on crystallinity. A model which is using a tensor for \( k \), which depends linearlily on the stress tensor was proposed by Van den Brule to consider the orientation
dependency, this model was extended by Zheng to account for crystallinity, but this extension is not very precise [72].

**Pressure-Volume-Temperature (PVT) Data**

Changes in temperature or pressure can lead to significant changes of the volume of thermoplastics. This is due to the expansion (isobaric change in volume due to temperature change at constant pressure) and the compressibility (isothermal change of volume due to change in pressure) of the material [72], [75]. This behaviour is usually displayed in so-called PVT-diagrams where the specific volume (the inverse density) is plotted over temperature for different levels of pressure (see Figure 9).

![PVT-diagrams for an amorphous and a semi crystalline Polymer](image)

*Figure 9: PVT-diagrams for an amorphous and a semi crystalline Polymer*

In these diagrams, amorphous materials usually show a change in the slope of the graph at the transition temperature of interest, which is the glass transition temperature. For semi crystalline materials, the melting temperature (or crystallization temperature, for heating or cooling respectively) is the transition temperature where the PVT-diagram shows an abrupt change in Volume [75]. This is due to the onset of Crystallization during cooling is regarded which will be discussed more in detail later in this chapter. For Injection moulding simulations, the modified Tait equation is widely applied to model the PVT-properties[72], [75]:

\[
\tilde{V}(p, T) = \tilde{V}_0(T) \left[ 1 - C \ln \left( 1 + \frac{p}{B(T)} \right) \right] + \tilde{V}_t(p, T)
\]

*Eq. 2-18*
Where \( C = 0.0894 \) is a constant,

\[
\bar{V}_0(T) = \begin{cases} 
(b_1^s + b_2^s (T - b_5), & \text{if } T \leq T_{\text{trans}} \\
 b_1^m + b_2^m (T - b_5) & \text{if } T > T_{\text{trans}} 
\end{cases}
\]

\text{Eq. 2-19}

Where a superscripted “s” indicates the solid and a superscripted “m” indicates the melt state of the polymer.

\[
B(T) = \begin{cases} 
 b_3^s \exp[-b_4^s (T - b_5)], & \text{if } T \leq T_{\text{trans}} \\
 b_3^m \exp[-b_4^m (T - b_5)], & \text{if } T > T_{\text{trans}} 
\end{cases}
\]

\text{Eq. 2-20}

and

\[
\bar{V}_r(p, T) = \begin{cases} 
 b_7 \exp[b_8 (T - b_5) - b_9 p], & \text{if } T \leq T_{\text{trans}} \\
 0 & \text{if } T > T_{\text{trans}} 
\end{cases}
\]

\text{Eq. 2-21}

where \( b_7, b_8 \) and \( b_9 \) are set to zero for amorphous Polymers, since Eq. 2-21 describes the exponential transition of semi crystalline polymers around the crystallization temperature. In Equations Eq. 2-19 to Eq. 2-21, \( T_{\text{trans}} \) is the transition temperature which is assumed to be a linear function of pressure:

\[
T_{\text{trans}} = b_5 + b_6 p
\]

\text{Eq. 2-22}

and \( b_1 \) to \( b_9 \) are fitting parameters [72], [75].

The compressibility (\( \kappa \)) of the material can be calculated from the Tait-model as

\[
\kappa = \frac{1}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial p} \right)_T
\]

\text{Eq. 2-23}

And the coefficient of volume expansion as:

\[
\beta = \frac{1}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial T} \right)_p
\]

\text{Eq. 2-24}

**Crystallinity**

Injection moulded semi-crystalline materials usually have an inhomogeneous structure over the cross-section of the part. As described in [78], [79] for isotactic Polypropylene, this structure is
composed of three characteristic main layers and two interface layers between them. Those layers are:

- Surface layer: this layer is characterized by low crystallinity, very fine crystals and a high nucleation rate. The surface layer is created when the hot melt comes in contact with the cool mould and solidifies instantly with a high cooling rate.
  - Transition layer: in this layer an oriented microstructure can be found. Lamellae, which grow from the nuclei in the surface layer, grow in the direction of the thermal gradient towards the centre of the part and are stretched and oriented in the flow direction by the high shear rates in this area. Because this area is still close to the mould, the temperatures are quite low and the cooling rate is high.

- Shear layer: the second main layer shows the so-called shish-kebab structure. The main molecule chains are highly stretched and oriented in the flow direction while regularly spaced lamellar structures, which surround the main chain annularly can be found.
  - Trans crystalline layer: bands of spherulites form on the linear sequence of the nuclei in the shear layer, which grow in the direction of the thermal gradient towards the core layer in the centre.

- Core layer: the third main layer in the centre of the cross-section. In this layer, mainly spherulite structures can be found. This layer has the lowest cooling rate, which enhances crystal growth. When the temperature drops below the crystallization temperature, nucleation starts followed by the nuclei’s development into spherulite crystals. The size of the spherulites depends on the cooling rate, the crystallization temperature and the injection moulding process conditions [78].
The morphology (or microstructure [74]) of injection moulded parts made from semi crystalline materials can, therefore, be described by the crystallinity (volumetric proportion of the crystalline compared to the amorphous phase), the size, shape, distribution and orientation of the crystallites and the orientation of the amorphous phase and filler materials. The morphology itself has a direct influence on the mechanical properties of the moulding. The crystalline areas are stiffer and stronger while the amorphous areas show higher toughness and flexibility [75].

The above mentioned layered structure and, therefore, the morphology of the moulding are influenced by the processing parameters. Especially the Cooling rate and the rheological history of the material play an important role for the development of the crystal structure [79]. The thickness of the surface layer mainly depends on the mould temperature [78], [79]. It decreases with increasing mould temperature. Menges, et al. [79] found an influence of melt temperature, packing pressure and injection speed (in order of descending influence) on the thickness of the surface layer, while Nguyen-Chung, et al. [78] (who did not use a packing phase in their investigation) found a decrease of the surface layer thickness with increasing injection speed only.

Both mentioned investigations found the shear layer to be thicker close to the gate and a reducing thickness in the filling direction. This was found to be in agreement with the simulated decrease in shear rate in [78]. The thickness of this layer is according to [79] reduced by an increased injection velocity, mould and melt temperature and decreased pressure (in order of descending importance).
These results are confirmed by [78], besides that they found an unchanged thickness of the shear layer when the mould temperature was changed.

The size and the amount of the crystallites in the core layer were found to depend mainly on the cooling rate and, therefore, on the processing temperatures since the shear rates in this area are usually quite low. Higher cooling rates lead to more but smaller crystallites, while bigger and fewer crystallites could be found at higher melt and mould temperatures [78], [79].

Many of the effects of the crystallization on the material properties are not well represented by the models used for simulation. Crystallization leads to a sharp increase in viscosity when the melt is cooling down, which is not considered in the Cross-WLF model. Most commercial simulation programs use a transition or no-flow temperature to model the transition from liquid to solid. This leads to a relatively small error for amorphous materials, but is a bigger problem when it comes to semi crystalline materials. In these materials, the so-called super-cooling effect can be found. This effect can lead to flow at temperatures below the no-flow temperature when the material is cooled at a high cooling rate. A high shear rate instead can lead to an elevation of the no-flow temperature. These effects can lead to a bad prediction of the flow pattern and the filling pressure and is critical for warpage and shrinkage prediction [72].

It is, furthermore, problematic for accurate simulation results to ignore the effects of the cooling rate on the specific thermal properties of semi crystalline materials. This can cause significant errors in the specific heat capacity of the material and the heat conductivity since both depend on the degree of crystallization. On top of that, the latent heat which is created when the material crystallizes is usually ignored in the simulation models [72].

In Autodesk Moldflow Synergy Insight (AMSI), a crystallization model presented by Zheng and Kennedy [80] was implemented. This is a first step towards more precise simulation of injection moulding with semi crystalline materials. In the 2016 version of the software, however, this model can only be applied for geometries meshed as dual domain or mid-plane models [81]. On top of that, there are very few materials, which are already characterized for the use of this model (33 out of 9610 grades, where the 9610 materials include all materials in the AMSI 2016 database) [82]. Therefore, it would be necessary to characterize the used material concerning the necessary parameters to use the crystallization model.

The model implemented in Moldflow describes the crystal-growth with the following equation [83]:

Where $G_0$ and $K_g$ are material grade-specific constants obtained from crystallization under quiescent conditions, $R_g$ is the gas constant, $U^*$ is the activation energy of motion,

$$T_{\infty} = T_g - 30$$  \hspace{1cm}  Eq. 2-26
With the glass transition temperature $T_g$,

$$f = \frac{T + T_{m}^0}{2T} \quad \text{Eq. 2-27}$$

Where $T_{m}^0$ is the material grade-specific equilibrium temperature, which depends on the pressure only:

$$T_{m}^0 = T_{eq} + b_6 p \quad \text{Eq. 2-28}$$

Where $T_{eq}$ is the equilibrium melting temperature, $b_6$ is a material specific parameter from the Tait-model and $p$ is the pressure.

The generation of nuclei is the sum of the number of nuclei activated under quiescent condition ($N_0$) and the nuclei induced by the flow ($N_f$). Further information can be found in [80], [83].

The effect of crystallization on the viscosity is implemented by an enhancement factor:

$$\frac{\eta}{\eta_a} = 1 + \frac{\left(\frac{\alpha}{A}\right)^{\beta_1}}{\left(1 - \frac{\alpha}{A}\right)^\beta} \quad \text{Eq. 2-29}$$

Where $\eta$ is the viscosity of the system, $\eta_a$ the viscosity of the amorphous phase, $\alpha$ the crystallization and the remaining parameters ($A, \beta & \beta_1$) are empirical.

Even though this crystallization model cannot be used for the simulations for the aforementioned reasons, it is expected to gain some insight by simulating the FIM-process. It is just necessary that one is aware of the limitations of the simulation results, when the crystallization effects are mainly ignored.

**Warpage and Shrinkage**

To simulate warpage and shrinkage of the moulding, the following material properties are necessary:

- Linear coefficient of thermal expansion (CTE)
- Elastic modulus
- Poisson’s ratio
- And the shear modulus

Due to the anisotropy in the injection moulded parts the CTE and the elastic modulus have to be determined for three orthogonal directions. For thin walled parts, which are typical for injection moulding, however, the thickness direction can be neglected [72].
2.4 Summary

This section presented the state of the art and the theoretical background of the most important technologies, processes and tools used in this PhD-project.

The working principle of a direct methanol fuel cell system was explained. The effects which deteriorate the system efficiency such as slow reaction kinetics, cross-over of reactants and CO₂ creation have been presented together with the recent research activities focusing on these problems. To improve the reaction kinetics, the research focus is on the development of new catalysts, the cross-over is addressed by the search for new membrane materials to be used as electrolyte in the MEA. A variety of venting solutions have been presented from literature.

The injection moulding process was presented as a process which is well suited for mass production and can be applied for a wide range of materials. The versatility of this process is also based on the presented special processes developed from the conventional injection moulding process. Processes that can reduce the amount of necessary assembly steps such as 2K-moulding and insert moulding are of interest for this project. Film insert moulding was the chosen process to produce the fuel cell container and will be described in chapter 3. Therefore, a more detailed state of the art review was presented on this process.

Injection moulding simulations can be used to identify possible problems in a mould design prior to the mould construction as well as for the investigation of unexpected moulding results and are, therefore, a valuable tool to save cost and time. The underlying physical models were presented in this section. Semi-crystalline materials were still found to be problematic for high precision simulation of warpage, even though a model for crystallinity was implemented in the latest version of the used software package, but only few materials were characterized for this model.
3. Injection moulding concept and material selection

This chapter describes the considerations for the implementation of the concept for the injection moulded fuel cell housing described in [38]. Theoretically all the processes presented in chapter 2.2.1 can be taken into consideration. Three designs with a porous, methanol repellent venting structure on the inside were identified to be suitable for the implementation of the container. These designs and the according processes and process chains were developed and evaluated and are presented here. Afterwards, the criteria for the selection of suitable materials and the final choice of the materials are presented.

3.1 Process selection

For the implementation of the fuel cell design given in [38], a porous structure on the inside of the container is needed. This structure has to be methanol repellent, which means that the contact angle between the solid surface and the liquid has to be at least 90°. Furthermore, a venting structure on the outside of the container is required.

Three concepts based on different processes were designed and evaluated (see Figure 11). Concept a) is based on an approach which combines 2K-moulding with structural foam injection moulding. The porous structure on the inside of the container can be created by using structural foam injection moulding, and especially the MuCell® process, which uses supercritical gases, is suited to create this structure with pore sizes in the µm range. Furthermore, it can be applied to all kinds of injection mouldable polymers [84]. In this process, typically closed pores and a solid skin layer are created [85], therefore, further modifications of this process have to be made to create a network of interconnected pores. One way to create interconnected pores is described by Kramscher, et al. in [86] where leaching particles are used to connect the pores and open the skin layer. Other possible ways use a large amount of the supercritical gas [87], or initiate the pore nucleation by slightly opening the mould after injection [88].

Methanol repellent surfaces are difficult to create due to the low surface energy of methanol. The super-hydrophobic properties needed can be achieved by implementing micro- and nanostructures in combination with materials with a low surface energy [89] or by using low surface energy coatings as presented in [90]. Afterwards the foamed part can be overmoulded with a second material to reduce permeability and to create the interface for mounting the fuel cell.

To obtain a proper intrusion pressure (as described later in section 3.2.1), the size of the pores should be as small as possible. For the method described in [86], the size of the interconnecting pores depends on the size of the leaching particles. For this concept, a suitable leaching material and a solvent would have to be found. Afterwards, a process would be necessary to blend the
Leaching particles homogeneously within the polymer. For fine powders, which are necessary in this case, an agglomeration of particles can be problematic for a homogeneous distribution. The leaching process is also critical due to the small surface of the leaching particles in contact with the solvent. Furthermore, the solvent would have to pass through the small pores to create interconnected pores throughout the entire part.

Wu, et al [87] described diameters of at least 40 µm for their method using polyurethane as polymer. These pore sizes are expected to be too large for the use in this application.

The method proposed in [88] could only be used in combination with a cavity transfer process, since the foamed part will be bigger than the actual cavity in the mould used for foaming due to the mould opening step. The foamed part would then be used as an insert in a second mould. This approach can be considered similar to the process design b) and c).

Due to the necessary leaching step or the use of a cavity transfer process, concept a) will lead to a longer and more complex process chain than the concepts b) and c).

For these reasons, concept a) was rejected.

The Concepts b) and c) use a similar approach. In both cases a microporous membrane, which is methanol repellent, is used. Membranes of this kind are commercially available. The difference in these two concepts is how the membranes are inserted. In concept b) a frame is used to keep the membrane in shape. The frame/membrane assembly can then be used as an insert part. Processes like thermoforming can be used to shape the membrane. For the frame, a punched and bent sheet metal can be used to which the membrane is attached by means of adhesives.
For the realization of concept c) the membrane is cut into the required shape and directly used as film insert. It is folded over the core of the mould and has to be kept in place during the filling phase.

The concepts b) and c) can be implemented in a standard injection moulding machine. Both of these concepts can be based on the same combination of membrane and overmoulding material. An overview of the decisive differences between both these designs is given in Table 3.

The main differences in this evaluation are related to the metal frame and the advantages and disadvantages of its use. Using insert moulding, on the one hand, has the advantage of a higher mechanical stability of the insert. This can avoid that the membrane is folding over when the insert is overmoulded. Furthermore, the fixation of the insert part inside the mould is easier to achieve, due to the stabilization of the frame compared to the film insert moulding design. When the flow direction of the overmoulding material is chosen, so that it presses the insert onto the core, an additional fixation of the insert part can even be unnecessary. Using a metal frame can also improve the mechanical stability of the whole container. The metal structure can increase the stiffness of the sidewalls and, therefore, reduce the deformation of the container when it is exposed to external forces. Another advantage of the membrane as insert part (as shown in Figure 11 b)) is that only the membrane is in contact with the fuel. Therefore, the requirements for the overmoulding material in terms of chemical resistance and permeability of methanol and water are lower than in design c).

On the other hand, design b) also shows some disadvantages. The process chain is way longer than in design c). While the membrane has to be cut into the according shape in design c) before it can be inserted in the mould, design b) requires more steps in the process chain. Additional to the cutting step, a frame has to be produced. This adds punching and bending of a sheet metal and the

Figure 11: Concept study for fuel cell container: a) 2K-foam moulding b) Insert-moulding c) Film insert moulding, Top row: Iso-view, middle: Cross-sectional view, bottom: Insert
assembly of the membrane (which possibly has to be pre-formed) on the frame to the process chain. When thermoforming of the membrane is used for pre-forming, the pores of the membrane could be stretched. A larger pore diameter would have an adverse effect on the intrusion pressure the membrane can withstand.

While there is only one existing interface in the film insert moulding design between the overmoulding material and the film insert, there are three in the insert moulding design. Adding interfaces (between the membrane and the frame and between the frame and the overmoulding material) increases the complexity of the material selection and the process. Insufficient adhesion at an interface can lead to delamination and, therefore, to failure of the whole part. For the insert moulding design, material selection and process parameters would have to be optimized for the optimum adhesion between the frame and the overmoulding material and the membrane and the overmoulding material. Additionally, a process would have to be found which guarantees a good adhesion of the membrane on the frame.

The use of the metal frame has further disadvantages: it increases the part weight compared to a continuous plastic sidewall and can be prone to corrosion when it is in contact with methanol or water.

By using a thicker insert such as the one of design b) compared to design c), the flow pattern will be more disturbed during the filling phase of the mould. A higher inhomogeneity in the cross-section of the flow channels can lead to a more pronounced flow hesitation in the sections with the smaller cross-section and consequently to weldline-formation or filling problems. This can result in a deterioration of the mechanical properties of the container. [91]

Due to the relatively long list of disadvantages, it can be concluded that concept b) implies more risks of part failure and expectable problems related to the manufacturing of the fuel cell container. The advantages of this design concept are mainly based on the increase in mechanical stability due to the mechanical properties of metal in comparison to plastics. These advantages are, however, outweighed by the importance of the advantages of concept c) for the use in hearing aids. The limited space in hearing aids favours a thin walled design. The weight reduction by foregoing the use of a metal frame will lead to a lighter system, which is more comfortable to wear behind the ear. A short process chain with fewer parts in the overall assembly allows for a more cost-effective production with fewer interfaces, which are typically critical to failure. On top of that, there are way fewer disadvantages expected with design c) where the disadvantage of the film insert fixation has only to be considered for the mould design. Once a suitable fixation system is found and successfully implemented in the mould, this is not a disadvantage for production anymore. Due to these reasons, concept c) was the concept implemented in the experimental part of this work.
Table 3: Pros and cons for concept choice

<table>
<thead>
<tr>
<th>Design</th>
<th>b) Insert moulding</th>
<th>c) Film insert moulding</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantages</strong></td>
<td>+ Frame offers higher mechanical stability of the insert</td>
<td>+ shorter process chain</td>
</tr>
<tr>
<td></td>
<td>+ Easier or no fixation of the insert necessary</td>
<td>+ lower material costs</td>
</tr>
<tr>
<td></td>
<td>+ Metal frame can increase mechanical stability of the entire container structure</td>
<td>+ thinner wall design possible</td>
</tr>
<tr>
<td></td>
<td>+ Methanol only in contact with membrane</td>
<td>+ lighter design</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+ less interfaces</td>
</tr>
<tr>
<td><strong>Disadvantages</strong></td>
<td>- Longer process chain</td>
<td>- Film insert has to be fixated in the mould</td>
</tr>
<tr>
<td></td>
<td>- Thermoforming process can stretch membrane and its pores and therefore reduce the methanol intrusion pressure</td>
<td>- Methanol in direct contact with overmoulding material</td>
</tr>
<tr>
<td></td>
<td>- Additional interface which can lead to delamination effects</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Metal increases part-weight</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Metal part can be prone to corrosion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Metal frame can lead to additional flow disturbance during the filling process</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Material Selection

Selecting “the best” material for an injection moulding process is challenging. First of all, there is a vast number of plastic grades available. In 2010 over 65,900 grades of mouldable and formable materials by around 500 suppliers were listed [92]. The most characteristic material properties for a large variety of polymers can be found in handbooks (e.g. [93], [94]). These books present data which is often neither directly measured nor can a reliable calculation for their properties be found and the data is typically based on semi-empirical models [73]. The use of filler materials and other additives like UV-stabilizer, flame retardants, plasticizers, etc. can have an influence on the material properties which can cause different properties for two grades of the same polymer. On top of that plastics show a much greater sensitivity to changes in the processing conditions than other materials and the part properties depend on both the intrinsic material properties and the processing conditions [73]. Typically, that leads to a range of values for a certain property instead of a single value. Furthermore, it is difficult to find reliable durability data. Properties such as the dimensional stability over time, the change in mechanical properties such as tensile and impact strength and fatigue behaviour in combination with environmental influences and the resulting aging of the plastic material and chemical resistance can typically, if at all, be found as a qualitative rating.
The selection of the materials for the fuel cell container focuses on the selection of a suitable venting membrane first. Besides the chemical resistance against methanol, the membranes have to show a methanol repellent surface and a certain intrusion pressure. The overmoulding material was chosen to achieve a good compatibility between the overmoulding material and the film insert. Obviously, this material has to be compatible with the injection moulding process. Furthermore, a sufficient chemical resistance against methanol is necessary. To minimize the methanol loss through the container walls, low methanol permeability is necessary. The mechanical properties of the materials have not been of primary interest in this selection. This is because there are no dimensional specifications given for design parameters such as wall thickness, etc. The design can be therefore done based on the chosen material instead of finding a material which can enable a certain design.

3.2.1 Membrane

During the operation of the fuel cell, $\text{CO}_2$ is created. The amount of $\text{CO}_2$ generated during the operation at the conditions presented in [22] with a continuous power output of $P = 2.5 \, \text{mW}$ at a Voltage of minimum $U = 350 \, \text{mV}$ for $t = 24 \, \text{h}$ can be found by Faraday’s law of electrolysis:

$$m = \frac{MIt}{zF} \quad \text{Eq. 3-1}$$

with

$$M = \frac{m}{n} \quad \text{Eq. 3-2}$$

and

$$P = U I \quad \text{Eq. 3-3}$$

follows by inserting Eq. 3-2 and in Eq. 3-1

$$n = \frac{It}{zF} = \frac{P}{U I} \frac{t}{zF} \quad \text{Eq. 3-4}$$

Where $m$ is the mass, $M$ is the molar mass, $I$ is the electrical current, $t$ is the time, $z$ is the valency number of ions of the substance, $F = 96485 \, \frac{C}{mol}$ is the Faraday constant, $n$ is the amount of substance, $U$ is the voltage [5]. In the methanol oxidation reaction (Eq. 2-1) per mole methanol one mole water is used, six mole electrons are transferred and one mole $\text{CO}_2$ is created. For the above-mentioned specifications for the fuel cell operation, this results in an amount of $1.066 \times 10^{-3} \, \text{mol} \, \text{CO}_2$ (and the same amount of methanol and water is used). Assuming CO$_2$ as an ideal gas under standard ambient temperature and pressure (SATP: $T = 298.15 \, \text{K}, p = 1 \, \text{bar}$) conditions, this corresponds, according to the ideal gas law:
\[ pV = nRT \quad \text{Eq. 3-5} \]

where \( R = 8.3145 \frac{J}{\text{mol} \cdot K} \) [5] is the ideal gas constant, to a volume of \( V_{\text{CO}_2, \text{gaseous}} = 0.026 \text{ l} \) generated during the operation time of 24 hours. The correspondent \( \text{CO}_2 \)-generation rate is therefore \( \dot{V}_{\text{CO}_2, \text{gaseous}} = 0.3 \frac{\mu l}{s} \). At the same time, methanol is consumed with a rate of \( \dot{V}_{\text{MEOH}} = 0.5 \times 10^{-3} \frac{\mu l}{s} \) and if a diluted methanol solution is used as fuel without any water management, the water consumption rate is \( \dot{V}_{\text{H}_2\text{O}} = 0.2 \times 10^{-3} \frac{\mu l}{s} \) according to

\[ \dot{V}_x = \frac{nM}{\rho_x t} \quad \text{Eq. 3-6} \]

Where \( x \) is the index for either water (\( x = \text{H}_2\text{O} \)) or methanol (\( x = \text{MEOH} \)) and \( \rho_x \) is the density at SATP (\( \rho_{\text{H}_2\text{O}} = 1 \frac{kg}{l} \) and \( \rho_{\text{MEOH}} = 0.79 \frac{kg}{l} \)) [65]. The volume of \( \text{CO}_2 \) generated is significantly higher than the volume which is available due to the consumption of water and methanol. To calculate the pressure in an unvented cell is, however, not that straightforward. System specific phenomena like methanol and water crossover as well as the rather negligible \( \text{CO}_2 \) crossover through the membrane of the MEA [95] increase the available space for the \( \text{CO}_2 \). On top of that \( \text{CO}_2 \) is soluble in methanol water mixtures, therefore, not all of the \( \text{CO}_2 \) will be in the gaseous phase [96]. For the design of the fuel cell container, however, the minimum acceptable \( \text{CO}_2 \) venting rate to avoid any pressure build up inside of the container was chosen as the volume of the \( \text{CO}_2 \) generated per second (0.3 \( \mu l \)). To avoid system failure when a peak current exceeds the average current and the venting rate of the system is, therefore, not sufficient anymore, an overpressure of 0.5 bar was assumed as the safety margin.

**Contact angle (CA)**

To provide the venting mechanism presented in [38], the membrane has to be methanol repellent. Especially for high concentrations of methanol, the surface tension of the fuel is significantly lower than for water. Thus, a surface which is just hydrophobic could be wetted by the methanol solution. Therefore, a so-called oleophobic surface is wanted. Oleophobic surfaces show contact angles of 90° and more in contact with liquids with a low surface tension. Typically hexadecane (surface tension of 27.5 mN/ m) is used as a reference liquid to test oleophobicity [97]. This corresponds to the surface tension of a methanol water solution of around 70 wt.-% methanol (\( \approx 17.3 \text{ mol/l} \)) at 25 °C [98]. Surfaces showing contact angles of more than 150 °C are considered as super-oleophobic. The contact angle between a homogeneous, smooth and flat surface and a liquid depends on the mechanical equilibrium between the surface tensions of the gas, the solid and the liquid, which are in contact at the three-phase boundary. This relationship is expressed in Young’s equation:

\[ \cos(\theta) = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad \text{Eq. 3-7} \]
Where $\theta$ is the contact angle, $\gamma_x$ is the surface tension of the liquid ($x = lv$), of the solid surface ($x = sv$) and of the liquid solid interfacial tension ($x = sl$).

Furthermore, the contact angle is influenced by the surface roughness of the solid surface. For moderate hydrophilic to hydrophobic surfaces, an increase in surface roughness increases the resistance of the surface to being wetted by the liquid. Hydrophilic surfaces can, however, be transformed into super-hydrophilic surfaces by increasing their surface roughness. The increase in hydrophilicity with an increase in surface roughness is classically described by the Wenzel equation:

$$\cos(\theta_w) = r \cos(\theta) \quad \text{Eq. 3-8}$$

where $\theta_w$ is the Wenzel angle, $\theta$ is the contact angle of the smooth surface and $r$ is the ratio between the actual and the projected surface area. For moderate hydrophilic to hydrophobic surfaces the influence of the roughness can be found by the Cassie-Baxter model. This model describes the liquid in contact with the peaks of the rough surface and a boundary to the air between the peaks:

$$\cos(\theta_{app}) = f \ast \cos(\theta) + (f - 1) \quad \text{Eq. 3-9}$$

with the apparent contact angle ($\theta_{app}$), and the area fraction of the solid $f$.

High oleophobicity can, therefore, be achieved with materials with a low surface energy, a surface texture roughness and a re-entrant geometry.

For the fuel cell container several commercially available membranes were investigated by contact angle measurements by the project partner at the Danish Technological Institute [99] for their suitability for the CO₂-venting structure. Therefore, at least 3 measurements were taken for each combination of membrane and wetting liquid. The results are presented in Table 4. For the contact angle measurement, a drop shape analysis system (KRÜSS DSA10-MK2) was used. The oleophobicity of these membranes is typically obtained using low surface energy materials such as PTFE or by using coatings, which create a low surface energy layer on the surface of the membrane. An overview over the tested membranes can be found in Table 4. Pore size values are taken from the producer’s datasheet.
Table 4: Different membrane types tested at the Danish Technological Institute [99]

<table>
<thead>
<tr>
<th>Distributor</th>
<th>Type</th>
<th>Pore size (single values are diameter sizes) in μm</th>
<th>Material</th>
<th>CA water in °</th>
<th>CA hexadecane in °</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pall</td>
<td>Versapor® R200</td>
<td>0.2</td>
<td>Acrylic copolymer membrane cast on a nonwoven nylon support</td>
<td>124 ± 3.9</td>
<td>101 ± 4.0</td>
</tr>
<tr>
<td></td>
<td>Versapor® R450</td>
<td>0.45</td>
<td></td>
<td>137 ± 1.1</td>
<td>111 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>Versapor® R800</td>
<td>0.8</td>
<td></td>
<td>145 ± 1.4</td>
<td>115 ± 3.0</td>
</tr>
<tr>
<td></td>
<td>Versapor® R1200</td>
<td>1.2</td>
<td></td>
<td>143 ± 2.0</td>
<td>123 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>Versapor® R3000</td>
<td>3</td>
<td></td>
<td>144 ± 0.1</td>
<td>120 ± 3.6</td>
</tr>
<tr>
<td></td>
<td>TF-200</td>
<td>0.2</td>
<td>PTFE with PP support</td>
<td>132 ± 3.1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Zefluor™</td>
<td>0.5</td>
<td>PTFE with PTFE support</td>
<td>140 ± 0.9</td>
<td>0</td>
</tr>
<tr>
<td>Porex®</td>
<td>PM22ST</td>
<td>6-10</td>
<td>PTFE</td>
<td>141 ± 1.4</td>
<td>110 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>PM3VT</td>
<td>8-8.62</td>
<td></td>
<td>149 ± 3</td>
<td>123 ± 2</td>
</tr>
<tr>
<td>Seal and</td>
<td>aspire® QBV657</td>
<td>1.7-2.12</td>
<td>Expanded PTFE (ePTFE) with polyamide support</td>
<td>131 ± 4.8</td>
<td>87 ± 7.1</td>
</tr>
<tr>
<td>Design</td>
<td></td>
<td></td>
<td></td>
<td>127 ± 0.6</td>
<td>95 ± 7.0</td>
</tr>
<tr>
<td></td>
<td>aspire® QP943</td>
<td>0.45</td>
<td>ePTFE with Polyester support</td>
<td>141 ± 4</td>
<td>106 ± 5</td>
</tr>
<tr>
<td>Clarcor</td>
<td>aspire® QP944</td>
<td>0.2</td>
<td></td>
<td>141 ± 4</td>
<td>106 ± 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>141 ± 4</td>
<td>106 ± 5</td>
</tr>
<tr>
<td>Chemplex®</td>
<td>Microporous PP</td>
<td>0.21x0.05</td>
<td>Polypropylene</td>
<td>108 ± 4.0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Gas permeable film</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Merck</td>
<td>FHUP04700</td>
<td>0.45</td>
<td>PTFE with high density polyethylene support</td>
<td>141 ± 3.1</td>
<td>0</td>
</tr>
<tr>
<td>Millipore</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SABEU</td>
<td>Traketch® PET23</td>
<td>0.22</td>
<td>PET with nonwoven PP support</td>
<td>124 ± 1</td>
<td>99 ± 1</td>
</tr>
</tbody>
</table>

2) No value was given in the datasheet. Pore size was calculated from Eq. 3-10, the CA with water and the water intrusion pressure from the datasheet.
The membranes listed in Table 4 which showed a contact angle of less than 90° for hexadecane were excluded from the selection. The Versapor® membranes showed a significant decrease in the contact angle within 24 hours when in contact with methanol and were therefore rejected [99].

**Pressure resistance**

An important criterion for the choice of the membrane is its intrusion pressure. This pressure is the minimum pressure required to initiate a flow through the porous structure of the membrane. The intrusion pressure can be found according to [100]:

$$\Delta P = \frac{4 \gamma_L}{D} \cos \theta$$  \hspace{1cm} \text{Eq. 3-10}

Where $\Delta P$ is the pressure difference across the membrane, $\gamma_L$ is the surface tension of the liquid, $D$ is the pore diameter and $\theta$ the contact angle. To be precise this equation requires round pores, but is used in the following section for an estimation of the intrusion pressure for methanol, since that value can typically not be found in the datasheets. To prevent leakage the minimum intrusion pressure has to be at least as high as the safety margin of 0.5 bar. A high intrusion pressure can be achieved by a small pore size in combination with a high contact angle. In the semi-logarithmic plot in Figure 12, the CA versus the pore diameter is plotted. High pressure differences can be obtained by small pore diameters and high CAs. Such a membrane could be found on the top left in Figure 12.

![Figure 12: Contact angle vs. pore diameter for selected membranes](image)

**Figure 12: Contact angle vs. pore diameter for selected membranes**
In Table 5 the absolute values of the methanol intrusion pressures for membranes with a CA of more than 90° are listed. The values for $\Delta P$ are typically negative due to its definition as the difference between the downstream pressure (in this case atmospheric pressure on the outside) and the upstream pressure (pressure inside the container). These values were calculated with the mean value of the CA of hexadecane and the datasheet values for the pore-size listed in Table 4.

Table 5: Methanol intrusion pressures

<table>
<thead>
<tr>
<th>Distributor</th>
<th>Type</th>
<th>$\Delta P$ in kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pall</td>
<td>Versapor® R200</td>
<td>104.94</td>
</tr>
<tr>
<td></td>
<td>Versapor® R450</td>
<td>87.60</td>
</tr>
<tr>
<td></td>
<td>Versapor® R800</td>
<td>58.11</td>
</tr>
<tr>
<td></td>
<td>Versapor® R1200</td>
<td>49.93</td>
</tr>
<tr>
<td></td>
<td>Versapor® R3000</td>
<td>18.33</td>
</tr>
<tr>
<td>Porex®</td>
<td>PM22ST</td>
<td>4.70</td>
</tr>
<tr>
<td></td>
<td>PM3VT</td>
<td>7.22</td>
</tr>
<tr>
<td>Clarcor</td>
<td>Aspire® QP944</td>
<td>151.60</td>
</tr>
<tr>
<td>Seal and Design</td>
<td>Aspire® QP943</td>
<td>21.30</td>
</tr>
<tr>
<td>SABEU</td>
<td>Traketch® PET23 B K320 D0,22 h PP50</td>
<td>78.22</td>
</tr>
</tbody>
</table>

To avoid leakage at pressures below 0.5 bar (50 kPa), the membranes by Clarcor and SABEU are, therefore, considered the best options. SABEU offers the Traketch membrane with another type of oleophobic coating, which is only produced in larger quantities upon request and, therefore, could not be tested. This coating would lead to an increase in the CA to hexadecane and, therefore, similar properties to the Clarcor-membrane are expected.

Typically, mechanical properties for these membranes are not tested by the supplier. Due to the typically small samples (DIN A5 to A4 sheets) received by the suppliers, the high costs and large minimum purchasing quantities, it was decided to choose a membrane without any a priori tests concerning the mechanical properties of the membranes.

3.2.2 Compatibility of membrane and overmoulding material

To achieve a good result in FIM, the film insert material has to be compatible with the overmoulding material. This concerns mainly the properties which influence the adhesion between the film insert and the overmoulding material. Furthermore, the film insert has to withstand the temperatures during the injection moulding process.

Adhesion

For the adhesion between polymers several mechanisms can play a role and are discussed in literature. Adhesive forces can be based on mechanical, chemical, diffusive, electrostatic or thermodynamic mechanisms [45], [101].

The mechanical mechanism is based on interlocking of the structures of the polymers. In overmoulding processes, this can be achieved by filling drafts or undercuts in the first component with the melt when it is overmoulded and lead to parts which are almost impossible to separate.
without destruction of the part [45]. When micro and nanostructures, such as the surface roughness, are being filled, the underlying mechanism is still discussed. In this case the adhesion could be caused by mechanical interlocking as well as the increase in the surface with an increase in surface roughness, which can lead to an increase in binding sites for other mechanisms [101].

The chemical mechanism is based on a chemical reaction at the interface between the two polymers and the creation of ionic, covalent or metallic bonds. Therefore, close contact at the interface, sufficient activation energy and materials suitable to react with each other are necessary. The electrostatic adhesion can be based on van der Waals forces or hydrogen bonds [101]. These forces are typically way weaker than chemical bonds [5].

The thermodynamic mechanism relates the adhesion to the wettability. According to the Young-Dupré equation:

\[ W_a = \gamma_l(1 + \cos(\theta)) \]  

the work of adhesion \( W_a \) can be determined by measuring the CA \( \theta \) between a liquid with a known surface tension \( \gamma_l \) and the surface with surface energy \( \gamma_s \). Several modifications of this equation exist for the calculation of the surface energy by separating \( \gamma_{sl} \) in Young’s equation (Eq. 3-7) into the contributing \( \gamma_l, \gamma_s \) and the dispersion (van der Waals) and the polar components. Another approach is based on an equation of state. A minimization of the interfacial energy between two polymers \( (\gamma_{sl}) \) leads to good adhesion, in other words: when the first component (solid) is readily wetted by the second (small CA) liquid component good adhesion can be achieved [101]. Furthermore, it is advantageous when the two polymers show similar surface tensions.

The diffusive or welding mechanism is based on the diffusion of polymer chains through the interface. Therefore, the polymers have to be in close contact and above their glass transition temperature. When both components involved are made of the same polymer, the adhesion mechanism is called auto-adhesion or self-adhesion. In this case the strength of the interfacial region is time dependent and can reach the cohesive strength if the interface is kept at a sufficient temperature long enough [102]. In overmoulding processes this time is typically shorter. Therefore the adhesion mechanism in overmoulded parts is rather based on the entanglement of sections of the polymer chains at the interface than on the diffusion of entire chains [45]. If the system consists of two different polymers, a further condition has to be satisfied, namely the compatibility of the two polymers. This can be estimated by solubility parameters. The smaller the difference between the solubility parameter of the solvent and the one of the solute, the better is the solubility of the solute in this solvent. The Hildebrand solubility parameter for substances of low molecular weight can be calculated by:

\[ \delta = \sqrt{\frac{\Delta U_E}{V_m}} = \sqrt{\frac{\Delta H_E - RT}{V_m}} \]  

where \( \Delta U_E \) is the change in the internal energy of evaporation, \( V_m \) is the molar volume, \( \Delta H_E \) is the enthalpy of evaporation, \( R \) is the ideal gas constant and \( T \) is the absolute temperature [103].
A more detailed model, the Hansen solubility parameter (HSP) model considers the contribution of atomic dispersion forces, molecular dipole-dipole forces and hydrogen bonds to the energy of evaporation. The HSP is given as the square root of the sum of the squares of the dispersion solubility parameter ($\delta_D$), the polar solubility parameter ($\delta_P$) and the hydrogen bond solubility parameter ($\delta_H$) as [104]:

$$\delta = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \quad \text{Eq. 3-13}$$

The solubility parameters for plastics can be found by testing them against a series of solvents with known $\delta_D$, $\delta_P$ and $\delta_H$. The more the polymer is affected by the solvent, the closer the solubility parameters are, which are then calculated by a software [104]. For overmoulding applications, the melt can be seen as solvent and the insert material as solute. The smaller the distance between the HSP between those two, the higher is the expectable affinity. To solve a material in a solvent, the free energy of mixing ($\Delta G^M$) has to be smaller or equal to zero:

$$\Delta G^M = \Delta H^M - T\Delta S^M \leq 0 \quad \text{Eq. 3-14}$$

where $T$ is the absolute temperature, $\Delta H^M$ and $\Delta S^M$ are the change in the enthalpy and the entropy of mixing respectively [104]. Using the Hildebrand solubility parameter, this condition leads to dissolution at material combinations with a difference in the solubility parameter below $6 \frac{MJ}{m^3}$ [73]. For the HSP this condition leads to a sphere with a radius $R_0$ in a 3D-plot where the axes denote the partial solubility parameters $\delta_D$, $\delta_P$ and $\delta_H$. The solubility distance $R_a$ between the materials is found by:

$$R_a^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2 \quad \text{Eq. 3-15}$$

where the indices 1 and 2 indicate the different materials. A ratio $\frac{R_a}{R_0}$ smaller than 1 indicates a high affinity between solvent and solute [104].

Typically, these parameters show a temperature dependency and most of the available data is based on a reference temperature of 25 °C. Nevertheless, Islam described a good correlation between the bond strength of the 2K-cavity transfer-moulded parts and the solubility parameters and concluded that the HSP found at 25 °C can be used for an initial estimation of the compatibility of two polymers in 2K moulding [45]. Due to the similarity between the cavity transfer process and the insert moulding applications, this is expected to be also valid for FIM.

Even though all these models can be used as an explanation for the adhesion effects, there is no model, which is generally valid for the description of adhesion [105].
Both membranes suitable for use in the fuel cell container according to the aforementioned criteria consist of a microporous polymer film, which is laminated a nonwoven support as shown in Figure 13. The nonwoven support layer can be a big advantage in terms of the film insert adhesion. When the overmoulding material fills the structures between the fibres, a strong mechanical interlocking can be achieved.

**Temperature**

Another important factor for the compatibility of the film insert and the overmoulding material are the temperatures during the moulding process. For good adhesion, a high interface temperature can be beneficial. A remelting of the insert material in combination with the increased mobility of the single polymer chains can lead to an improved entanglement at the interface and, therefore, to better adhesion [45]. On the other hand, both membrane layers are made out of film materials, which can contain residual stresses. At elevated temperatures these stresses can start to anneal, which can cause dimensional changes in the film layer [106]. An ideal temperature, therefore, would be sufficiently high to achieve a low viscosity of the overmoulding material to fill the gaps between the fibres of the support layers, re-melt the surface of the fibres to enable chain entanglement across the interface, but low enough to not influence the membrane material. The interface temperature can be calculated according to Eq. 5-11

Another important temperature for the prototype production is the mould temperature. The film insert is inserted manually in the mould. The inserts are relatively small and have to be inserted precisely. If the required mould temperature is too high, this can be problematic for the insertion of the membranes.

### 3.2.3 Overmoulding Material

The main purpose for the overmoulding material is to offer sufficient mechanical stability for the container. This property, however, is achieved by the combination of material properties and part design and was, therefore, not considered for the selection of the material, since the part design can be adapted to the chosen material. The focus in this section is, therefore, on material properties which cannot be changed by the design such as: suitability for the injection moulding process, chemical resistance, barrier properties to restrict the methanol loss through the container and the compatibility to the film insert.
**Process suitability**

The first limit for the material selection is based on the chosen process. The amount of suitable materials is limited by the obvious restriction that the material has to be processed by injection moulding.

**Chemical Resistance**

The main purpose of the injection moulded part is to form the methanol container for the fuel cell. It is, therefore, constantly in contact with water and methanol. The material property related is the chemical resistance. If the chemical resistance is not good enough, the part can suffer from chemical degradation. Chemical degradation is a constitutive material property, which is typically predicted qualitatively. Methods for numerical estimation of the chemical degradation do not exist at the moment and the degradation rates are typically defined indirectly by measurements of other physical quantities like stress relaxation. Chemical degradation can have a drastic, negative influence on mechanical properties of a polymer such as tensile, elongation and impact strength and resilience. Furthermore, it can cause discoloration and yellowing [73]. Unlike physical effects, like swelling, which can be reversible, chemical degradation is irreversible. Chemical degradation of Polymers is based on chemical reactions which can break down the polymer chains and, therefore, reduce the molecular weight, which deteriorates the mechanical properties or on the reaction of the attacking chemical with the chemical bonds of the functional groups, which can, for example, lead to a lower degree of entanglement. Elevated temperatures typically increase the influence of solvents on polymers [92].

Amorphous polymers and amorphous regions in semi-crystalline polymers are more prone to chemical attack than the crystalline phase. In general, excellent chemical resistance can be found with: Fluoroplastics, Polymides, Polyolefins, Acetals, Polyphenylene Sulphide, Allyls, Epoxies, Ionomers, Polyamide-Imide [92]. In general, it can be stated that polar solvents show a higher interaction with polar polymers and non-polar solvents with non-polar polymers. For semi-crystalline polymers, chemical attack typically occurs at temperatures close to the melting temperature with solvents of similar solubility parameters [92]. The liquids which can act as solvents in the fuel cell container are water and methanol. While water is highly polar, due to the electronegativity difference between oxygen and hydrogen, methanol is mainly polar. Therefore, non-polar semi-crystalline polymers can be expected to show good chemical resistance. Non-polar polymers typically consist of either symmetrical molecule chains or atoms with a low difference in electronegativity [5].

**Environmental influences and Environmental stress cracking**

Environmental influences can decrease the mechanical stability of polymers. This can occur due to UV-radiation where the absorbed energy can break most single covalent bonds, strong bonds like O-H and C-H bonds, however, are not affected. Most pure organic polymers (e.g. PE, PP, PVC, PS, etc.) do not absorb UV-wavelength. Impurities and structural defects, however, can lead to absorption, which can lead to degradation of the material and embrittlement. The effect can be reduced by UV-absorbing additives. Oxidation of Polymers is typically an effect which is only critical after a long time. In combination with the photochemical effect described before, a synergetic effect can be found in the so-called photo-oxidation. This effect can lead to discolouration and mechanical degradation of some polymers. To reduce this effect, anti-oxidant additives can be used [73].
Environmental stress cracking describes a phenomenon where parts made out of polymer materials fail at stress levels way below their yield strength in the presence of an organic vapour or liquid. This can happen even though the polymer does not solve or swell in this organic substance, due to an interaction of physical influences and mechanical stress and can even be caused by residual stresses in moulded parts. The part failure can then be caused by breaking (environmental stress cracking) or by a multitude of very fine cracks known as crazes (environmental stress crazing). These phenomena can be found in amorphous and semi-crystalline materials [73].

**Permeability**

Permeability describes the passage of gases and liquids through another material such as a solid. The permeability depends on the solubility of the mobile media in the solid and its diffusion rate through it. It can therefore be found as:

\[
P = -D S \quad \text{Eq. 3-16}
\]

where \(P\) is the permeability, \(D\) is the diffusion coefficient and \(S\) is the solubility coefficient. The transport of molecules of the permeant can be described by three steps. At the beginning, the permeant absorbs at the polymer surface (adsorption), followed by the transport through the bulk material by diffusion and is finally released at the other surface of the bulk material by desorption. The mass transfer rate can be found by Fick’s first law of diffusion:

\[
\dot{m} = -D A \rho \frac{dc}{dx} \quad \text{Eq. 3-17}
\]

where \(\dot{m}\) is the mass transfer rate, \(A\) is the surface area, \(\rho\) is the density of the solid material, \(\frac{dc}{dx}\) is the concentration gradient across the thickness of the bulk material. By integration and with:

\[
c = S p \quad \text{Eq. 3-18}
\]

where \(p\) is the pressure, Eq. 3-17 becomes

\[
\dot{m} = -D S \rho A \frac{p_1 - p_2}{L} = P \rho A \frac{p_1 - p_2}{L} \quad \text{Eq. 3-19}
\]

where \(L\) is the thickness of the solid material. For amorphous polymers, the influence of the pressure on the permeability can be taken into account by the Henry-Langmuir model [44]. In this model, the concentration of the sorbed substance reaches a saturation at high pressures [73]. For liquid permeants, the solubility can be found by using the value for the corresponding saturated vapour. Characteristic permeability coefficients for a permeant-polymer system can only be obtained when no interaction (such as e.g. swelling of the polymer) can be found for the system, otherwise the behaviour is more complex and a permeability range rather than a single value can be found [93].
Furthermore, permeation is temperature dependent. The sorption, the diffusion and, therefore, permeability, too, follow an Arrhenius type behaviour and increase with increasing temperatures [44].

The permeability coefficient is mainly determined by the chemical structure of a polymer, which defines the magnitude of the permeability coefficient. It is, however, influenced by the morphology of the polymer and by physical factors, like: density, crystallinity and orientation.

In general, it can be stated that the smaller the free volume in the material, the lower the permeability. Therefore, materials with a high density show low permeability. The ordered structure in the crystallites of semi crystalline materials reduces the permeability significantly compared to the corresponding amorphous areas, therefore, a high degree of crystallinity leads to low permeability. A reduction in the permeability can also be found in parts with a high orientation of the molecules [93].

The part thickness has typically a nonlinear effect on the permeability. Initially, the permeability decreases with thickness, but reaches a plateau at a critical thickness. For thin parts, the surface structure has a significant influence on the permeability [92].

The chemical affinity of the polymer for the permeant has a strong influence. Polar groups in the polymer, for example, lead to an interaction with water molecules, which strongly affect the equilibrium sorption and the diffusivity, while the sorption of water for hydrophobic (nonpolar) polymers such as polyolefins follows Henry’s law (Eq. 3-18) [73].

For the fuel cell container, an ideal material would show a high permeability for CO₂ and a low permeability for water and methanol.

3.2.4 Selection

Based on the two membranes (Clarcor and SABEU) which are suitable for use in the fuel cell container according to the selection criteria presented above, an overmoulding material must be found. Based on the support material, the adhesion can be expected to be good when the gaps in the nonwoven structure can be filled. Using a material which is similar to the support material in terms of the solubility parameters can enhance the adhesion further. The material grades used for the support layers are, however, unknown and were not revealed by the suppliers. While at least the polymer type is known for the SABEU-membrane (polypropylene), the polyester support of the Clarcor-membrane indicates a whole family of polymers containing e.g. polyethylene terephthalate (PET), polybutylene terephthalate (PBT) or polycarbonate (PC). Even though the conducted tests showed that the Clarcor-membrane performed better, the SABEU-membrane was chosen for the prototype production. This choice has several reasons. First of all, the available information concerning the support material is more specific. Besides that, the membrane is already meeting the requirements, the performance is expected to be better with the more oleophobic coating, which is available on request. A different coating on the membrane will influence the membranes’ performance, but won’t have significant influence on the process. For the investigation of the film insert moulding, the membrane characterized above can be used and be replaced by the one with the better coating for production, when necessary. And finally, fluoropolymers such as the PTFE used in the Clarcor-membrane have a negative environmental impact, due to the strong covalent
bond between the fluorine and the carbon atoms. This bond provides the excellent chemical resistance of these polymers and the high thermal stability, on the downside this leads to negative impacts on the environment [107]. Even though the coating material of the SABEU-membrane is not revealed by the producer and might contain fluoropolymers, too, the amount of fluorinated material would be considerably lower.

The chosen SABEU-membrane is made of a 23 µm thick PET-membrane and a non-woven layer of polypropylene fibres as support. The total nominal thickness of this film is 200 µm ± 20 µm according to the datasheet. The nonwoven support has a weight of 50 g/m². The air flow rate for this membrane is 3.5±0.5 l/ (min cm² bar).

To choose the overmoulding material, suitable materials were chosen based on their chemical resistance against water and methanol. Therefore, the rating in [92] was used, which is based on a summary from various sources such as supplier datasheets and research papers. The rating is based on a scale from 0-10 based on the percentage of weight change, the change in a characteristic length, the volume change and the percentage of the change in mechanical properties such as tensile strength, elongation modulus, flexural strength and impact strength, where 0 indicates the polymer being solved in the solvent and 10 indicates almost no change to no change at all. For methanol and water, none of the listed polymers reached a level of 10. Therefore, all the polymers showing a chemical resistance of 9 were considered for the next level of the material selection. These materials can be found amongst the polymers: Polyoxymethylene (POM, both homo and copolymer), cellulose propionate (CAP), ethylene vinyl alcohol copolymer (EVOH), polyethylene (PE; including linear low density PE (LLDPE), low density PE (LDPE) and high density PE (HDPE)), polyamide (PA; PA6 and PA66), polycaprolactones (PCL), PC, polycycloolefin (COC), polyethylene terephthalate (PET), polypropylene (PP), high impact poly styrene (HIPS) and polyvinylidene chloride (PVDC). The data has, however, to be handled with care since it is not based on standardized tests and based on data of different material grades, processing conditions and so on.

In the next step, these polymers were investigated concerning their permeability. The data given for permeability can also vary in a range, depending on test conditions, used material (typically film materials are of primary interest for the packaging industry) and so on. On top of that, permeability for very few permeants can typically be found. While gases such as O₂ and CO₂ are investigated quite often and water vapour permeability is also easy to find, the permeability of methanol vapour is barely to be found. Qualitative statements can be found more readily on most of the aforementioned polymers.

PA-polymers are hygroscopic, which leads to a relatively large water uptake and to swelling, which increases the free volume between the polymer chains and deteriorates the barrier properties of the material [73], [108]. These materials were, therefore, rejected in this selection just as EVOH for the same reason.

PC offers in general rather poor barrier properties and was excluded as well. For some of the materials mentioned above no data could be found.
According to [108] and [109], the low water vapour permeability is found for PP, PVDC and HDPE, followed by PET. The permeability data for CO\textsubscript{2} and O\textsubscript{2} can be found in Figure 14. The error bars indicate the range, which can be found in the data collected in [110]. The large ranges, for example, for PP are based on the measurements of a wide range of grades and types of the chosen material such as oriented films, co-polymers, etc. The values for HIPS, COC and PBT are based on single material tests. High gas permeability can be found for PP, PE, HIPS and COC. A high permeability to CO\textsubscript{2} can have a positive influence on the venting behaviour of the system, even though the contribution will be negligible due to the small surface area of the container. Estimating the surface area inside the container (\approx 200 mm\textsuperscript{2}), which is entirely in contact with CO\textsubscript{2}, neglecting the film insert and an overpressure of 0.5 bar inside of the container made out of PP (using the mean value in Figure 14) this will lead to a permeation rate of $1.6 \times 10^{-3} \frac{\text{ml}}{s}$ which is about 5 \% of the CO\textsubscript{2} created per second. The oxygen permeation into the container could affect the methanol oxidation reaction at the anode. The driving pressure would be the partial pressure of oxygen in the air which is about 21\% of the atmospheric pressure according to Dalton’s law. The low pressure in combination with a permeability which is typically lower than that of CO\textsubscript{2}, the Oxygen permeation can be considered as negligible.

![Figure 14: Permeability coefficients for CO\textsubscript{2} and O\textsubscript{2}](image-url)
Data on methanol permeability, however, could only be found for PP, HDPE and LDPE and is presented in Table 6. As for the chemical resistance data, this can only be used for an identification of possible material candidates.

Table 6: Permeability coefficient for Methanol [93]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature in °C</th>
<th>Permeability [P]= g mm/ m² day</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE</td>
<td>21.1</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>54.4</td>
<td>10.9</td>
</tr>
<tr>
<td>HDPE</td>
<td>22.8</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>48.9</td>
<td>2.0</td>
</tr>
<tr>
<td>PP</td>
<td>22.8</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>48.9</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The total surface area in the container which is in contact with methanol can be estimated to be around 200 mm². As presented in chapter 4, the container wall thickness was chosen as 0.75 mm. Assuming a closed container made out of, for example, PP the estimated methanol loss through the container walls at 48.9 °C for one recharging cycle would be 400 µg or approximately 0.5 µl and, therefore, only 2.5 ‰ of the filling volume.

The HSP were calculated using the data offered in [104]. According to the author, some of the data used might be questionable. Furthermore, it might relate to specific material grades, which are not necessarily injection mouldable. Therefore, it is seen as a further indicator for the material selection, supporting the chemical resistance data. $R_a/R_0$ ratios were calculated for the interaction of the polymer with water, methanol and the membranes support material (PP). While a high value for this ratio is wanted for water and methanol (low solubility) for good chemical resistance, a low value for the PP indicates a possibly good adhesion. The values are shown in Table 7

Table 7: HSP for chosen Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\delta_p$ in MPa$^{1/2}$</th>
<th>$\delta_H$ in MPa$^{1/2}$</th>
<th>$R_0$</th>
<th>$R_a/R_0$ $\text{CH}_3\text{OH}$</th>
<th>$R_a/R_0$ $\text{H}_2\text{O}$</th>
<th>$R_a/R_0$ PP</th>
<th>Material reference number in [104]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDC</td>
<td>20.4</td>
<td>10</td>
<td>10.2</td>
<td>7.6</td>
<td>2.14</td>
<td>2.12</td>
<td>2.40</td>
</tr>
<tr>
<td>PA6</td>
<td>17</td>
<td>3.4</td>
<td>10.6</td>
<td>5.1</td>
<td>2.98</td>
<td>3.61</td>
<td>1.73</td>
</tr>
<tr>
<td>PA66</td>
<td>17.4</td>
<td>3.4</td>
<td>14.6</td>
<td>5.1</td>
<td>1.83</td>
<td>2.29</td>
<td>2.80</td>
</tr>
<tr>
<td>POM</td>
<td>17.1</td>
<td>3.1</td>
<td>10.7</td>
<td>5.2</td>
<td>2.95</td>
<td>3.59</td>
<td>1.72</td>
</tr>
<tr>
<td>EVOH</td>
<td>20.5</td>
<td>10.5</td>
<td>12.3</td>
<td>7.3</td>
<td>2.03</td>
<td>2.09</td>
<td>2.70</td>
</tr>
<tr>
<td>HDPE</td>
<td>18</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>12.22</td>
<td>12.85</td>
<td>0.17</td>
</tr>
<tr>
<td>PP</td>
<td>18</td>
<td>0</td>
<td>1</td>
<td>6</td>
<td>4.21</td>
<td>4.38</td>
<td>0</td>
</tr>
<tr>
<td>PC</td>
<td>18.1</td>
<td>5.9</td>
<td>5.1</td>
<td>9.5</td>
<td>2.03</td>
<td>2.04</td>
<td>1.20</td>
</tr>
<tr>
<td>PET</td>
<td>19</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>4.07</td>
<td>4.15</td>
<td>1.12</td>
</tr>
<tr>
<td>HIPS</td>
<td>20</td>
<td>5</td>
<td>1</td>
<td>7</td>
<td>3.51</td>
<td>3.42</td>
<td>1.07</td>
</tr>
<tr>
<td>COC</td>
<td>18</td>
<td>3</td>
<td>2</td>
<td>5</td>
<td>4.61</td>
<td>4.7</td>
<td>0.53</td>
</tr>
</tbody>
</table>
According to the HSP, a good affinity to the PP of the support material can be found for COC, HDPE and PP in ascending order. The chemical affinity to water and methanol is the worst for HDPE, followed by COC and PP.

Considering all the aforementioned points, PP is a good choice for the overmoulding material. It has the highest affinity to the support layer; the highest CO\textsubscript{2} permeability and sufficiently low methanol permeation can be expected. Furthermore, it shows a low chemical affinity to water and methanol, which should lead to low or no swelling of the polymer.

Furthermore, PP has excellent resistance to environmental stress cracking [111].

For comparison, the selection of the overmoulding material was repeated by using the software “CES EduPack 2015” by Granta Design. The Level 3 Polymer database was used, which contains data of 750 generic polymer grades. Different limits were set similar to the approach presented before. Stage 1 was the ability to processing the material in injection moulding. Then chemical resistance to methanol and water was set and a maximum mould temperature of 60 °C to enable manual insertion of the film. This reduced the number of suitable polymers to 21 grades, including three PA11, three HDPE, a LDPE, a LLDPE, a PET, nine PP, two HIPS and one PVC (polyvinylchloride).

Plotting the Young's modulus vs. the density shows another advantage of PP that was not considered as a criterion for the material selection. PP typically offers a high E-modulus to density ratio, which is beneficial for light-weight design (see Figure 15) [112].

To ease the filling of the gaps of the non-woven structure, a PP grade with a high melt flow rate was chosen (SABIC 579S). The recommended processing temperature range for this material reaches from 15-20 °C to 50-60 °C for the mould temperature and barrel temperatures between 190 °C and 270 °C [113]. The interface temperature between the film insert and the melt can be calculated by Eq. 5-11. Assuming similar thermal penetration coefficients for the PP of the support layer and the overmoulding material, the insert being at mould temperature or slightly below, the core of the melt being at barrel temperature and the melt hitting the film insert with an 90° angle, so that the core layer hits the membrane and the highest temperatures for both the melt and the mould the resulting interface temperature is 165 °C. The melting temperature for polypropylenes can typically be found in the range of 112 °C and 208 °C [73]. This shows that a remelting of the surface of the support layer is, in general, possible with the chosen material combination, but does not happen in every case.
3.3 Summary

In this chapter, the material selection was described. The main criteria for the film insert were the methanol repellent properties and the intrusion pressure. For the overmoulding material, the chemical resistance, the permeability properties and the compatibility with the support material of the film insert were decisive. Finally, the SABEU membrane was chosen as the film insert and PP as the overmoulding material. The chosen membrane meets the requirements for the intended use and its non-woven support can lead to good adhesion between the film insert and the overmoulding material. Polypropylene as an overmoulding material is resistant to most commonly found chemicals (including methanol) and shows a low tendency to environmental stress cracking. Its permeability properties for water and methanol were found to be sufficiently low. Furthermore, it is the same polymer as used in the support layer of the membrane and can therefore lead to good adhesion.
4. Mould Design

In this chapter, the mould design is presented. To test the material combination, a mould-insert was designed which could be used in a set-up for in-mould visualization.

A second mould was designed to produce the fuel cell containers. This design is based on the container design presented in chapter 1 and 2. For prototype production, this design was based on the idea to allow for fast and inexpensive changes for some key factors of the container design.

4.1 Mould insert design for testing the FIM material combination

The mould inserts designed for the use in the in-mould visualization set-up are shown in Figure 16. This insert is used on the movable mould half and contains all the structures related to the filling such as the runner and the gate, the cavity itself and a 200 µm deep recess to insert and align the film insert. A CAD-file of the insert on the fixed half can be found in Figure 16. This insert creates a flat surface to close the structures in the movable half and a sapphire window, which can be used for in-mould visualization in combination with a high-speed camera. An exploded view of the entire mould assembly can be found in Figure 17. A mirror with an angle of 45° to the surface plane of the insert on the fixed half is installed in a cut out section of the clamping plate of the fixed mould half. This enables the use of a high-speed camera from the sidewall of the mould as shown in Figure 18.

The part produced with this mould is disc-shaped. The disc has a diameter of 17.25 mm and a thickness of 500 µm. In the centre of this disc, a 5 mm wide membrane strip was overmoulded, which covered the whole diameter in length (as shown in Figure 19). The dimensions of the film insert blank are shown in Figure 20. The film inserts were laser cut and inserted into the mould as shown in Figure 16. The membrane was aligned and fixated by double sided adhesive tape in the recess.

Figure 16: Mould inserts. Left hand side: Insert for fixed half (CAD-model), middle: Insert for movable half, right hand side: Insert for movable half with inserted film insert (CAD-model)
outside of the cavity (areas marked red in Figure 16). In addition to that, the membrane is clamped between the two mould halves (red and blue sections in Figure 16).

*Figure 17: Mould for in-mould visualization. Picture courtesy of Dr Ben Whiteside, RKT Centre Polymer MNT, University of Bradford, UK*
4.2 Mould for fuel cell container prototyping

4.2.1 General design considerations

The part design was based on the schematic shown in chapter 1. This is due to several reasons. First of all, the shape and the dimensions at the open side of the container were given by the design of the fuel cell, which has to fit in this section. The shape of this section was maintained to avoid
variations in the wall thickness. Variations in the wall thickness can lead to differences in the effect of the packing pressure in the different sections of the part because of an extended cooling time of the thicker sections. This can cause residual stresses or an increased warpage of the part. The stresses can reduce the mechanical stability of the part [106]. The container design and the according dimensions are shown in Figure 21.

A split-mould was used to realize holes for the CO₂-venting function on two of the sidewalls (see Figure 22). Split moulds offer a second parting plane orthogonal to the primary parting plane. When the mould is opened, the movable mould-half is separated from the fixed mould half in the opening direction of the machine. At the same time, the angle pins are opening the splits in the direction perpendicular to the primary parting line. This secondary parting plane enables the use of pins, which are protruding from the cavity’s sidewall. In the closed mould these pins are pressing on the film insert to create a hole in the overmoulded structure. A side-effect of this is that the film insert is additionally fixated by these pins during the filling. In the open mould, the fixation of the film insert is done by an under-pressure created by a system of channels implemented in the core structure, which was connected to a vacuum pump. The movable half of this mould is shown in Figure 23.

The sprue puller was designed according to the recommendations in [106].

A full round runner design was implemented to provide the best surface to cross-section ratio. The better this ratio, the less heat will be exchanged between the melt and the mould. This leads to a smaller proportion of the frozen layer in the runner and, therefore, to a smaller pressure drop compared to runner designs with a comparable cross-section. In addition to the low surface to cross-section ratio, a circular channel provides the lowest pressure drop per material used [114].
The gate was implemented as a pinpoint gate in the centre of the side opposite to the opening of the container. This gate position was chosen to enable a symmetrical radial filling of the part. Placing the gate at the chosen wall has further advantages. By utilizing this design, jetting effects are avoided, since the longest distance available for a free flow of the polymer is the wall thickness of the part [106]. This is important since the gate diameter, which was chosen as 80% of the wall thickness (=600 µm), can lead to high shear rates and, consequently, to a low viscosity of the melt, which is critical for jetting. The flow direction resulting from the gate position presses the film insert onto the core and, therefore, doesn’t counteract the insert fixation but rather works in its favour. In literature for the design of conventional injection, the typical recommendation for the diameter of a pin point gate is 40 to 50% of the wall thickness. For a miniaturized, thin walled part like the fuel cell container, this would lead to a significantly high pressure drop and high shear rates, which can be problematic for filling and a quick gate freeze off, which would avoid a proper packing phase. Even with a gate diameter of 80% of the wall thickness, de-gating will be possible without affecting the container wall. The gate is tapered towards the part with the smallest cross-section at the part, to avoid excessive post-processing of the part to remove the residues of the gate.

For the ejection of the part, a stripper plate around the core was used. This has the advantage that the ejection force is distributed equally along the face at the top of the container. The clearance, which is necessary to move the stripper plate, encloses the core structure and can be used for venting of the cavity. This mould offers two parting planes, which can also be used for venting. On top of that, the vacuum system in the core creates an active venting structure during the filling phase. For these reasons, no specific venting structure was necessary.
The structures for the mould temperature control were designed as straight channels for water or oil heating in the chase bolster of the fixed mould half and the splits retainer plate in the movable half. As a second option, electrical heater cartridges can be inserted in the chase bolster and the core retainer plate. Implementing a good temperature control in a split mould is rather challenging due to the movable parts and the resulting assembly tolerances, which represent a further thermal contact resistance to the thermal resistance of the mould steel and therefore deteriorate the heat transfer. Even though the heat transfer is expected to be worse between the movable parts of the mould than the heat conduction in bulk material, the temperature control had to be integrated at the mentioned positions due to the limited space in the splits.

A trade-off between part stiffness, low permeability and the injection pressure needed to fill the part on one side and a minimization of the part dimensions has to be found for the wall thickness of the container. A thicker wall will create a stiffer part with less deflection in case of a pressure built up in the system, provide lower permeability and reduced injection pressures. Instead a smaller wall thickness improves the ratio of system volume to stored methanol volume and reduces the weight of the system. For a rough estimation of the suitability of this wall thickness, a FEM-simulation was conducted using COMSOL Multiphysics 5.2. The film insert was modelled by a 1 mm x 1 mm x 23 µm patch of PET above the venting hole and a 100 µm thick PP-layer to model the support layer. Since the PP-layer does not take any of the mechanical properties and the expected anisotropy of the non-woven material into account, this model can only be used for an approximation of the order of magnitude of the stresses and deflections in the fuel cell container. The pressure safety margin chosen for the intrusion pressure of 0.5 bar was applied on the inside of the container. And the top surface of the container as shown in Figure 21 was set as fixed constrain. The simulation results can be found in Figure 24 and Figure 25.
According to the simulation results, the maximum deflection is expected in the centre of the sidewalls and in the low µm range (see Figure 24). The maximum stresses can be found in the corners of the part and around the venting-hole and will be in the low MPa range (see Figure 25). The yield strength of the chosen PP is 37 MPa according to the datasheet [115]. Therefore, the chosen wall thickness of 750 µm is sufficient for the mechanical stability of the fuel cell container.

4.2.2 Flexibility for quick changes in Prototyping

The mould was designed to make changes in the design lead to the least expenditure possible. This includes changes in the part-design as well as changes in the material selection. The modular concept of the design aims at the largest possible flexibility in prototyping without the need for redesigning and processing the entire cavity structure. Therefore, prototypes can be produced with the same technique as in mass production while the mould is prepared for expectable design changes.

One of these is the size, the amount and the position of the venting holes. To create the venting holes, an array of five pins (standard ejector pins with a diameter of 800 µm) was used in the splits. The pins can be inserted in through holes from the backside of the splits and are fixated by a lid (see
Figure 22, detail c). The amount and position of the holes can be adjusted by selecting the size of these ejector pins, which are inexpensive standard parts. If the pins are longer than the through-hole section in the split and long enough to press on the film insert, a venting hole will be created in the container at the position of this pin. If the pins level with the cavity wall, a closed surface will be created at this position. Figure 26 shows two of the possible combinations, where in a) all five pins are set to create a venting hole while in b) a venting hole in the centre of the container will be created. The area of the venting holes and therefore the CO₂-venting rate of the container can be adjusted by reducing the diameter of the protruding section of the pins. For bigger holes, the through-hole diameter would have to be increased, which requires a more expansive reprocessing of the splits. Therefore, rather big pins of 800 µm in diameter were chosen for the initial set up. In combination with the chosen membrane, this venting-hole size leads to a venting rate of $1.17 \frac{\mu l}{s \text{ mbar}}$. This is about a factor of four higher than the necessary venting rate of $0.3 \frac{\mu l}{s}$ when the overpressure inside of the container is as low as one millibar. Therefore, it is expected that the venting-hole diameter can be reduced in future iterations of the container design drastically. For the minimum size of the venting-hole, however, the mechanical load on the protruding pin during the filling phase and the venting rate must be considered. The design, furthermore, allows for the test of the influence of the venting hole position, 3 different distances from the fuel cell surface were implemented and a position centred on the sidewall can be tested against off-centre positions.

![Figure 26: Different pin combinations for the creation of CO₂ venting holes](image)

If a membrane of a thickness different than the chosen one is to be used, a new set of pins cut to the according length is sufficient to adjust the mould for that.

The heating system was designed in a way that a large variety of overmoulding materials can be used. Therefore, both a liquid based system and one based on electrical cartridges were considered in the design. This provides a wide range of possible mould temperatures even though high mould temperatures are problematic in terms of the manual insertion of the membrane. By using a combination of both liquid and cartridge based mould temperature control, the mould could be used in a variotherm moulding set-up.
Furthermore, the core insert can be replaced for changes in the wall thickness and the storage volume of the final container part. This, however, is more elaborate and time consuming than the pin replacement. The change of the outside dimensions of the container and the changes in the runner and the gate system can be achieved by a redesign or a replacement of the splits.

4.3 Summary

In this section, the two mould designs which were developed for film insert moulding were presented. For the initial material testing, a mould insert for a disc-shape part was modified to insert the film. The according mould can be used in an experimental set up suitable for in-process monitoring.

The mould design for the fuel cell container is based on a split mould design. The additional parting line can be used to create CO₂-venting holes in two of the sidewalls. A system of vacuum channels was implemented in the core insert for the fixation of the film insert. The modular design of the mould enables changes in some key-features of the part design without an excessive amount of reworking.
5. Experimental work

The experimental part of this work can be split into two main topics. The first part is an in-detail investigation of the suitability of the chosen materials for film insert moulding. This was done using different techniques to investigate an effect found for this material combination, namely the creation of blisters at the surface of the film insert. The second part is the validation of the mould design for the fuel cell container, which was presented in chapter 4.2. In addition to the experiments, simulations were conducted.

5.1 Film Insert Moulding-Blister characterization

For this series of experiments, the material combination presented in chapter 3.2 was investigated regarding its suitability for the use in FIM-processes. The mould presented in chapter 4.1 was used for this purpose. The membrane was inserted in the mould and subsequently overmoulded. For the moulding experiments, a Wittmann-Battenfeld Micropower 15 micro injection moulding machine was employed. This machine uses a screw (diameter: 14 mm) for plastification of the material and an injection plunger with a diameter of 5 mm for injecting the material. The first moulding experiments showed that the membrane could not be separated from the overmoulded part by hand, since the membrane broke before delamination occurred. Therefore, it was concluded that improving the adhesion between the film insert and the moulded part by optimizing the moulding parameters, concerning the adhesion, would not reduce the probability of failure in the moulded containers. It can be expected that the strength of the membrane would cause a destruction of the container, before the membrane delaminates from the moulded part, when the container is under pressure. For some combinations of the moulding parameters, however, blister creation at the surface of the film insert was observed. The underlying effects for the blister creation were investigated by means of in-process monitoring, CT-scans, surface metrology and process simulations.

5.1.1 Experimental set-up

A Full Factorial Design of Experiments (DOE) analysis was used to investigate the influence of the injection moulding parameters mould temperature ($T_{mould}$), barrel temperature ($T_{barrel}$), injection speed ($v_i$) and packing pressure ($P_{pack}$).

The levels for the parameters used in the DOE can be found in Table 8. The barrel temperatures were chosen to cover the temperature ranges given in the processing datasheet for the used Polypropylene [113]. The entire mould temperature range suggested in the datasheet could not be implemented, because the mould temperature control was based on electrical heating cartridges. This set-up did not allow for temperatures below room temperature. A temperature in the middle of

---

3 A table with the settings for the single runs can be found in the appendix
the suggested $T_{\text{mould}}$ range was therefore used as low level. A mould temperature of 60 °C is recommended in the Datasheet for thick walled parts, but is used in these experiments to cover the range of recommended values as good as possible. To reduce the number of experimental runs, only two levels for the mould temperature were chosen. This decision is based on a paper by Chen, et al. [64]. They found that the influence of mould temperature on warpage, crystallinity and crystal size shows a linear behaviour using PP in FIM. Therefore, a linear influence of $T_{\text{mould}}$ is expected in these experiments.

$P_{\text{pack}}$ was chosen as 40 %, 55 % and 70 % of the maximum injection pressure according to the processing datasheet. According to the conducted simulations, the highest injection pressures can be expected at Run 2 and Run 8. The process parameters of Run 2 were chosen, and the injection pressure at switch over was determined experimentally as 180 bar. The packing pressure levels for the DoE were chosen accordingly. For each experimental run of the DOE, five parts were moulded. Hereby, the following procedure was used:

- Short shots to define the switch over point for the current set of moulding parameters
- Moulding of five parts without the film insert to stabilize the moulding conditions
- Moulding one part with the film insert
- Five Repetitions of the two previous steps, so that five parts with the film insert were obtained for each run

Table 8: Injection moulding parameters for DOE analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low level</th>
<th>Medium level</th>
<th>High level</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{mould}}$</td>
<td>40 °C</td>
<td>-</td>
<td>60 °C</td>
</tr>
<tr>
<td>$T_{\text{barrel}}$</td>
<td>200 °C</td>
<td>235 °C</td>
<td>270 °C</td>
</tr>
<tr>
<td>$V_f$</td>
<td>100 mm/s</td>
<td>200 mm/s</td>
<td>300 mm/s</td>
</tr>
<tr>
<td>$P_{\text{pack}}$</td>
<td>72 bar</td>
<td>99 bar</td>
<td>126 bar</td>
</tr>
</tbody>
</table>

The short shot approach was chosen to constantly switch over when a certain percentage of the part was filled. The switch over point was defined as the point when the flow front covered the whole edge of the membrane according to the fill pattern found in the simulation. This fill pattern represents a filled volume of 98% of the total part volume (see Figure 27). Due to the manual insertion of the film insert the process could not be run fully automatically. Therefore, the stabilization step was introduced. Furthermore, a long mould open time of 30 s was necessary to have enough time for the insertion of the film, which led to very long cycle times. In a fully automated process, the cycle time can be drastically reduced and the stabilization step would not be necessary.

The packing time was set to four seconds throughout the set of experiments. This is long enough to guarantee a frozen gate. The maximum time for the gate freeze off found in the simulations was below three seconds. Therefore, the packing time will have no influence on the experimental results. An additional cooling time of three seconds was used to assure that the entire part is solidified. An influence of these two parameters can therefore be excluded.
For the evaluation of the DoE, the areal surface roughness parameters $Spk$ and $Smr1$ (see section 5.1.4 for explanation) were investigated. The DoE was evaluated for each of the surface roughness parameters respectively. All five parts per run were evaluated in terms of $Spk$ and $Smr1$. For each run, the mean value of these five parts for $Spk$ and $Smr1$ respectively was considered as one observation. This procedure allows for an evaluation of the standard deviations of these mean values, the so-called within run variability, additionally to the evaluation of the influence of the process parameters on the mean values. The evaluation of the standard deviations can show the influence of the chosen process parameters on the within run variability and by that identify the set of parameters that would lead to the most stable process [116], which is not necessarily the process with the best result concerning the avoidance of blister creation.

The DoE was used to find a regression model that represents the influence of the process parameters on the chosen areal surface roughness parameters. Therefore, a so-called stepwise approach is applied. This method adds or removes a parameter to a regression model based on the chosen $\alpha$-level. A factor with a P-value which is lower than the chosen $\alpha$-level is considered significant and added to the regression model. Factors with P-values which are higher than $\alpha$ are removed. If a factor which is not significant is part of a significant interaction, it is kept in the model to obtain a hierarchical model. Furthermore, the adjusted mean square (MS) value for the factors can be used to compare the influence of factors. This value represents how much of the variation of the regression model is explained by a single degree of freedom of a factor. The higher this value is, the stronger is the influence of the according parameter. A table with the order of the DoE-runs and the according process settings can be found in the appendix.

### 5.1.2 Simulation set-up

Virtual overmoulding experiments were conducted using the AMSI 2016 “in-mould label overmoulding” feature. This feature can be used for inserts with a thickness of less than 1 mm. The film insert (also known as in mould label) in this analysis has to be modelled separately from the actual moulding and is then considered by the software in terms of its influence on the flow and cooling behaviour [83].

![Figure 27: Fill pattern and Pressure at the switch over point. From left to right: Run 2, Run 7 and Run 30 (Processing Parameters can be found in the appendix)](image-url)
In this work, the CAD-model used for the simulation included the mould, the heating system in the form of heating cartridges, a sapphire window as the mould insert, the moulding and the film insert.

A multi-scale mesh was applied for the discretization of the model. This mesh type has the advantage that the element size can be adjusted according to the size and importance of the features of the model. This means that critical areas and small features can be meshed with a finer mesh, whereas, for example, a coarser mesh can be chosen in parts of the mould where a uniform temperature distribution can be assumed. This approach has, compared to a homogenous mesh size, the advantage that the number of elements is lower than in a homogenous mesh with a high mesh density and is more accurate than a coarse homogenous mesh. This can reduce the computation time of the model without affecting the accuracy in the critical areas. The differences in the mesh size can be seen in Figure 28, where the mesh density increases from the mould to the disk-shaped mould insert and further on towards the moulded part and the membrane (see Figure 29).

The mould, the mould inserts, the heating cartridges and the moulded part are discretized by using tetrahedral elements for the 3D-mesh type. For the film insert, a dual-domain has been chosen.
It is not possible to assign the in-mould label properties to the film insert when it is meshed using the 3D-mesh. While for micro moulding parts the 3D-approach is recommended [43] and an accurate representation around the film insert is wanted for which the 3D-mesh is recommended [117], the film insert itself is a thin walled part without any changes in thickness with part length and width being more than 10 time the film thickness. For this geometry, the dual domain model is appropriate [117]. By using this approach, the film insert is modelled as a thermal insulation while its thermal mass is neglected. Therefore, it is recommended to use this approach for thin film inserts only.

The chosen analysis sequence contained cooling, filling and packing and warpage analysis. On top of that a venting feature was implemented to take the venting of the mould into account. The recess for insert fixation is expected to act as a venting channel; therefore, a node in this area was chosen to model the venting channel. For the width and length of the venting channel, the values of the recess were assigned. Since the film insert is placed in the recess during moulding, an assumption for the height of the venting channel was made. According to the density of the non-woven support layer, the relation between the PP and the air in this layer is about 1:2. The venting channel won’t be just a rectangle with the according height (approximately 2/3 of the recess height), as it consists of an unknown number of smaller channels of different shapes due to the distribution of the PP-fibres. In this case, the air would be vented through these smaller channels, which are considered as a network of hydraulic resistances in parallel. The PET-membrane layer is expected to not contribute to the air flow in the venting direction. The remaining channel height therefore was estimated as one fourth of the height related to air, which equals 30 µm. The proportional distribution of the different layers is shown in Figure 30.
Model of the film insert

For these simulations, the membrane was modelled as a 200 µm thick PP foil. The material “Generic PP” was used as membrane material. This material is well characterized by Autodesk and was chosen as a representative Polypropylene, since the actual PP-grade used for the non-woven support layer was not revealed by SABEU. This model is a simplification of the real membrane, since the thin PET-layer is neglected as well as the non-woven character of the support layer. The reasons for these simplifications are based on the model creation for the simulation software. While the PET-layer can be added easily in a CAD-model, it causes problems for choosing the right mesh density for the insert. Since the ratio of edge length to thickness of the PET-layer is extremely large (217.4 for the membrane width and up to 1205.7 for the length of the overmoulded strip), meshing these areas would either lead to a high number of mesh-elements which would result in a long computing time or in too high aspect ratios for the single elements. This can affect the accuracy of the simulation. The reasons for not considering the non-woven character of the Polypropylene layer are similar. Modelling a non-woven fabric would have let to numerous single PP fibres with a high aspect ratio between the fibre diameter and the fibre length. This would result, just like the low aspect ratio of the PET-layer, in either a long computing time due to the number of elements, a bad representation of the layer due to too large minimum element size, or high aspect ratios.

Additionally, there is not much data on the membrane available. The only data revealed by the producer is an areal density of the support layer of 50 g/m², which could be used in combination with the given thicknesses for the membrane and the support layer (see chapter 3.2.4) and the density of the representative PP used to model the membrane to estimate the ratio between air and PP in the non-woven support. Furthermore, there was no data revealed on fibre diameters in the non-woven support, thermal properties of the membrane, etc., which would be necessary to create a more accurate model of the film insert. Therefore, the simplification of the film insert as a 200 µm thick PP-foil is taken as a starting point for the simulation. It is expected that this simplification could cause a deviation from the behaviour found in the real experiments mainly due to two reasons:

- Deviations in the thermal conductivity
- Deviations related to the filling behaviour of the non-woven support layer
In Figure 31, the thermal conductivity for the generic PP and the generic PET from AMSI 2016 is shown. For a one dimensional steady state heat transfer problem, this could be used to calculate the difference in the thermal resistance for a model of the membrane including the PET-layer and without it to estimate the error caused by this simplification. For this calculation, the analogy of an electronic circuit can be used. The thermal resistance in this case can be calculated as:

\[
R_{th} = \frac{d}{A k} \quad \text{Eq. 5-1}
\]

where \(A\) is the surface area through which the heat flow occurs, \(R_{th}\) is the thermal resistance, \(d\) is the thickness of the layer in the direction of heat flow and \(k\) is the thermal conductivity [118]. The difference in the thermal Resistance between modelling the membrane including the PET-layer and the PP model for a stationary one dimensional case would be:

\[
\Delta R_{th} A = \left| \frac{d_{pp}}{k_{pp}} - \left( \frac{d_{pp}'}{k_{pp}} + \frac{d_{PET}}{k_{PET}} + R_c \right) \right| \quad \text{Eq. 5-2}
\]

where the first term of the difference is the thermal resistance of the PP model and the term in brackets is the thermal resistance of the model including the PET-layer. For the last-named model, the thermal resistance is combined of the thermal resistance of the PP-support \(\left( \frac{d_{pp}'}{k_{pp}} \right)\) that of the PET-layer \(\left( \frac{d_{PET}}{k_{PET}} \right)\) and the contact-resistance between those two layers \(R_c\), which are connected in series. Using the average thermal conductivity, calculated from Figure 31 according to [118]:

\[
k_{\text{average}} = \frac{\int_{T_1}^{T_2} k(T) \, dT}{T_2 - T_1} \quad \text{Eq. 5-3}
\]

and
\[ d_{PP} = d_P - d_{PET} \quad \text{Eq. 5-4} \]

the difference between the two different models is

\[ \Delta R_{thA} = |2.7 \times 10^{-8} \frac{m^2K}{W} - R_c| \quad \text{Eq. 5-5} \]

As boundary temperatures \( T_2 \) and \( T_1 \), the melt and the mould temperature are used respectively.

The contact resistance usually can be found to be between \( 5 \times 10^{-6} \frac{m^2K}{W} \) and \( 5 \times 10^{-4} \frac{m^2K}{W} \). Since the thermal contact resistance decreases with decreasing surface roughness and increasing interfacial pressure [118], it can be expected to be in the lower region of the aforementioned interval. This is due to the low surface roughness of polymers and the assumption that two laminated polymer foils have a large contact area. Furthermore, it can be assumed that the interfacial pressure is high, at least during the filling phase, when the cavity pressure is acting on the film insert. The maximum error in the thermal resistance caused by neglecting the PET-layer would be around 30%. Delaunay and Le Bot found values for the thermal contact resistance between PP and a steel mould in the range of \( 5 \times 10^{-4} \frac{m^2K}{W} \) during the filling phase and up to \( 3.5 \times 10^{-3} \frac{m^2K}{W} \) during the cooling. Assuming these values, the error of the simplification of the membrane model can be up to 76% during the cooling phase.

The more critical simplification is to model a PP-foil instead of the non-woven PP fibres. A model for the thermal conductivity for fibrous materials was found in [119] and used in [120]. In [121] the model is modified to consider, among other things, the contact resistance between the fibres. Even though this model was originally used to model materials for building insulation, it seems legit to use the original model in the version of [120], since it calculates the thermal conductivity of the material based on the conductivity of the fibre material and that of air, the volumetric ratio of the two and a factor which depends on fibre orientation:

\[ k_{\text{non-woven}} = k_{PP} + \frac{k_{air} - k_{PP}}{1 + \frac{f}{1-f}\left(1 + \frac{2(k_{air} - k_{PP})}{k_{air} + k_{PP}}\right)} \quad \text{Eq. 5-6} \]

where \( f \) is the volumetric fraction of the solid material, \( k_{air} \) is the thermal conductivity of air and \( z \) equals 2/3 for random fibre orientation [120]. Using the \( k \)-values found by Eq. 5-3 and Figure 31, this leads to a thermal conductivity of \( 0.0631 \frac{W}{mK} \). This is about 1/3 of the thermal conductivity of PP \( (0.181 \frac{W}{mK}) \). Therefore, the model would underestimate the thermal resistance of the membrane by a factor of around 3.

However, these values can only be taken as estimations of the error done by the simplification of the film insert for the simulation model. First of all, because one of the assumptions for Eq. 5-6 is that the fibrous insulation layer (in this case the non-woven support layer) “can be approximated as a
homogenous medium of thermal conductivity [121]. This approximation is very doubtful for the dimensions of the film insert used in this experiment. The support layer is most likely too thin to assume a homogenous medium since there are not enough layers of fibres. This leads to a local variation of the number of layers within the plane of the flow direction, too. This variation can lead to local differences in the heat conduction, which could be a reason for blister creation that will not be considered by the simulation.

On top of that, there are a couple of effects which are not considered in Eq. 5-6. One of them is that highly drawn, semi-crystalline fibres can have a much higher thermal conductivity in the direction they have been drawn due to molecular orientation [44]. Another effect which is not considered is that there is a non-ideal contact between the single fibres, for these contacts an additional contact resistance would have to be added, which is one of the improvements of Eq. 5-6 in [121]. Furthermore, the thermal conductivity could be higher if the gaps between the fibres were filled with the overmoulding material and the air was replaced with polymer (see Figure 31).

The steady state assumption, however, is not true for injection moulding. The polymer melt is cooling instantly at the mould walls during the filling phase to create a frozen layer, which acts as a thermal insulation. At the same time, the melt at the interface, between this solid layer and the moving melt experiences high shear rates, which heat up the melt [106]. Therefore, the thermal conditions in this fountain flow behaviour are transient and can vary locally depending on e.g. structures in the mould. The heat conduction in injection moulding is usually considered as a one dimensional heat transfer problem perpendicular to the mould walls since injection moulded parts are typically designed as thin walled parts [40]. Assuming this one dimensional heat flow, the model of a semi-infinite solid can be used for the analysis of the cooling behaviour of the melt according to [118]:

\[
\frac{T(x, t) - T_i}{T_{\infty} - T_i} = erf c \left( \frac{x}{2\sqrt{\alpha t}} \right) - \exp \left( \frac{ht}{k} + \frac{(h^2 \alpha t)}{k} \right) \left[ erf c \left( \frac{x}{2\sqrt{\alpha t}} + \frac{h\sqrt{\alpha t}}{k} \right) \right]
\]

Eq. 5-7

where

\[
erfc(\xi) = 1 - \frac{2}{\sqrt{\pi}} \int_0^\xi e^{-u^2} du
\]

Eq. 5-8

is the complementary error function, \(x\) is the spatial variable for a position in the melt, \(\alpha\) is the thermal diffusivity, \(h\) is the heat transfer coefficient (htc) between the mould and the melt, \(t\) is the time after the first contact between the melt and the mould at that point, \(T_{\infty}\) is the mould temperature, \(T_i\) is the melt temperature and \(T(x, t)\) is the temperature at position \(x\) at the time \(t\).

Assuming perfect contact between the melt and the mould and therefore htc→∞, Eq. 5-7 is reduced to [118]:

\[
\frac{T(x, t) - T_i}{T_{\infty} - T_i} = erf c \left( \frac{x}{2\sqrt{\alpha t}} \right)
\]

Eq. 5-9
Solving Eq. 5-9 for \( x \) when \( T(x, t) \) equals the no-flow temperature of the used material, the thickness of the frozen layer \( (s_{\text{frozen}}) \) can be approximated as:

\[
s_{\text{frozen}} = 2 \frac{T_{\text{no-flow}} - T_i}{T_\infty - T_i} \sqrt{\alpha t} \tag{Eq. 5-10}
\]

The interfacial temperature \( (T_C) \) between the melt and the mould or the film insert as\[40]:

\[
T_C = \frac{(b_A T_A + b_B T_B)}{b_A + b_B} \tag{Eq. 5-11}
\]

\( T_A \) and \( T_B \) are the initial temperatures of the melt and the mould/ film insert respectively.

Where the thermal penetration \( (b_x, x = A, B) \) is given as:

\[
b_x = \sqrt{\frac{k \rho c_p}{\alpha}} \tag{Eq. 5-12}
\]

where \( \rho \) is the density and \( C_p \) is the specific heat capacity.

For precise results, however, it is inevitable to use numerical methods for the calculation of the thermal effects. Not only because parameters like density, thermal conductivity and the specific heat capacity in thermoplastic polymers are temperature dependent but also because the heat transfer coefficient between the mould and the melt is finite and changes within the process. It increases with decreasing cavity pressure and when the part shrinks away from the mould, which leads to a lower contact area and insulating air in the gaps between the contact areas. In simulation software like AMSI, this has been taken into consideration and therefore different htc values are used for the filling, the packing and the cooling phase. When using the insert moulding function, an additional htc is introduced by the software between the mould and the insert [122]. To compensate for the uncertainties and problems arising from misestimating the thermal resistance of the insert, a sensitivity analysis of this parameter could be used to find the best fit between the simulation and the experimental results in a re-engineering approach.

**Summary “Model of the film insert”**

The simplifications which were necessary to model the film insert for the use in AMSI2016 underestimate the thermal resistance of the film insert. The presented estimations show that the thermal resistance is expected to be 300\% - 400\% higher when the non-woven properties and the PET-layer would be considered than for the model used in the simulations. These estimations are based on steady state assumptions and further effects influencing the thermal conduction are not taken into consideration. This estimation, however, shows that the effect of the inserted film is underestimated in the simulations and therefore effects influenced by the film insert such as inhomogeneous cooling conditions and therefore warpage and shrinkage are expected to be found way more pronounced in real experiments than in the simulation results.
5.1.3 In-Process-Monitoring and interface investigation

To investigate the origin of the blistering, CT-scans and In-process monitoring were used. For the CT-scans, a NIKON XT H 225 computed tomography system was used and scans were taken from a badly blistered specimen and one which did not show blisters to identify the location of the origin of the blisters in this layered specimen (substrate - support layer - membrane).

The moulding cycle was observed through a Sapphire window in the fixed mould half using a high-speed camera (MEMRECAM HX-3 by nac IMAGE TECHNOLOGY). These videos were used to figure out during which part of the moulding cycle the blistering occurs. A big advantage of this method is that the whole moulding cycle can be analysed and compared to the results of the simulation. Without this tool, the parts of the moulding cycle where the mould is closed cannot be analysed visually. This information might allow a conclusion to be drawn about the reason for the emergence of the blisters. This information could hardly be gained by other means like surveillance of the cavity pressure or the cavity temperature. Using the high-speed camera enables the comparison of the shape of the flow front between the simulation and the experiment and can, therefore, reveal information on the accuracy of the representation of the flow front in the simulation. Due to the thin membrane layer, the filling of the non-woven structure and the onset of the blister emergence can be monitored with the high-speed camera. These effects are not necessarily visible in the data, which would be obtained from temperature or pressure sensors inside the cavity. This flow front comparison would not be possible utilizing temperature or pressure sensors. Another option would be to use an infra-red camera, which would give additional information about the melt temperature. In this case, however, the “Retardation-induced temperature drop”[64], which was described in section 2.2.3 could lead to a delay in the captured flow front under the membrane. For a more detailed investigation however, temperature and pressure sensors could be used in the cavity in addition to the in-mould monitoring using the high-speed camera.

5.1.4 Metrology

To characterize the degree of blistering of the membrane surface, an area of 5 x 10 mm² in the centre of the disk-shaped part was measured using an OLYMPUS LEXT 4100 confocal laser scanning microscope in stitching mode in combination with post processing in SPIP™ image metrology software by Image Metrology A/S (version 6.4.3).
The measurements were taken using the 10x magnification lens (10x MPlanFLN). The choice of this lens was a trade-off between having a large share of background noise (10x magnification lens and lower) due to the low numerical aperture and a drastic increase in measuring time (20x magnification and higher) due to a small field of view and an increased number of pictures necessary to cover the measurement area in the stitching mode. The background noise is believed to be mainly speckle noise, which can be found when coherent light is reflected from a rough surface (height variation of the surface is larger than λ/4, where λ is the wavelength of the light) [123]. Since the appearance of speckle patterns also depends on the numerical aperture of the observation optics (optics with a higher numerical aperture can resolve higher height variations) [123] and the objectives with higher magnification do have a higher numerical aperture, this noise can be reduced by choosing a higher magnification objective. Due to the large number of parts to be measured, however, and the large size of the blisters compared to the surface roughness of the PET-Membrane, a lower magnification level was chosen in combination with a noise filter in the post-processing step.

Table 9: Specifications of LEXT 4100 lenses

<table>
<thead>
<tr>
<th>Lens</th>
<th>Field of view</th>
<th>Working distance</th>
<th>Numerical aperture</th>
<th>Magnification</th>
</tr>
</thead>
<tbody>
<tr>
<td>5xMPlanFLN</td>
<td>2560x2560 µm²</td>
<td>20 mm</td>
<td>0.15</td>
<td>108x-864x</td>
</tr>
<tr>
<td>10xMPlanFLN</td>
<td>1280x1280 µm²</td>
<td>11 mm</td>
<td>0.3</td>
<td>216x-1728x</td>
</tr>
<tr>
<td>20xMPlanAPON</td>
<td>644x644 µm²</td>
<td>1 mm</td>
<td>0.6</td>
<td>432x-3456x</td>
</tr>
<tr>
<td>50xMPlanAPON</td>
<td>256x256 µm²</td>
<td>0.35 mm</td>
<td>0.95</td>
<td>1080x-8640x</td>
</tr>
<tr>
<td>100xMPlanAPON</td>
<td>128x128 µm²</td>
<td>0.35 mm</td>
<td>0.95</td>
<td>2160x-17280x</td>
</tr>
</tbody>
</table>

A comparison between the measurements taken with the objectives from the 5x to the 20x before and after filtering with a median 15x 15 full filter can be found in Figure 33, Table 10 and Table 11. The unfiltered measurement obtained with the 50x objective is presented as a reference. This lens has the highest numerical aperture (the same as the objective with the highest magnification)
The pictures in Figure 33 are showing that the noise decreases drastically with an increase in the magnification. Less noise in the unfiltered picture leads to a smoother representation in the filtered pictures. To compare these findings, five measurements of a single blister, which fitted the field of view of the 50x objective, were taken with each of the four objectives. The average values and standard deviations can be found in Table 10 and Table 11 for unfiltered and filtered measurements respectively. The values are given in the form of: Average value of five measurements ± Standard deviation.
Table 10: Lens comparison unfiltered

<table>
<thead>
<tr>
<th>Lens</th>
<th>Smr1 /%</th>
<th>Spk /µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5x</td>
<td>10.55 ± 0.70</td>
<td>13.05 ± 2.52</td>
</tr>
<tr>
<td>10x</td>
<td>11.98 ± 0.48</td>
<td>3.60 ± 0.61</td>
</tr>
<tr>
<td>20x</td>
<td>22.25 ± 0.14</td>
<td>3.79 ± 0.02</td>
</tr>
<tr>
<td>50x</td>
<td>18.11 ± 0.15</td>
<td>3.22 ± 0.02</td>
</tr>
</tbody>
</table>

The noisy surface in the unfiltered measurements leads to large differences in the measurements between the single objectives.

Table 11: Lens comparison filtered

<table>
<thead>
<tr>
<th>Lens</th>
<th>Smr1 /%</th>
<th>Spk /µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5x</td>
<td>7.61 ± 2.14</td>
<td>2.52 ± 0.32</td>
</tr>
<tr>
<td>10x</td>
<td>16.69 ± 0.49</td>
<td>2.43 ± 0.11</td>
</tr>
<tr>
<td>20x</td>
<td>22.38 ± 0.13</td>
<td>3.70 ± 0.02</td>
</tr>
<tr>
<td>50x (unfiltered)</td>
<td>18.11 ± 0.15</td>
<td>3.22 ± 0.02</td>
</tr>
</tbody>
</table>

After filtering the differences between the measurements which were obtained by the 10x objective, the 20x objective and the 50x objective are smaller. Only the measurements which were taken with the 5x magnification lens is showing a result far from the other three measurements. The Smr1 value for the 10x objective is closer to the one of the reference measurement with the 50x objective and the difference for the Spk value is below 1 µm. The repeatability of the 10x objective is lower than for the 20x, but the standard deviation is low enough for the expected values of at least several µm for Spk and around 10 % for Smr1. Therefore, the 10x objective was used, which provides way shorter measurement times.

A 5 x 10 mm² size area was measured using the stitching function of the microscope (see Figure 32). The stitched picture consisted of 5 x 10 pictures with 20 % overlap between the single pictures. The “fine” mode for acquisition was employed, which utilizes a vertical step of 2 µm between the single acquisitions with the 10x objective.

The post processing contained the following steps using the built-in functions of the metrology software:

- First order levelling: compensate for tilt (built-in function: Global levelling)
- Second order levelling: compensate for warpage of the specimen (built-in function: Global bow removal)
- Median 15x15 full filter: compensate for optical noise especially speckle patterns
- Definition of an Area of interest (AOI) which contained the actual width of the film insert only
- Zero Background height: set the most frequent height as zero level
- Calculation of the surface roughness parameters
The calculation of the surface roughness parameters by the software is done according to the ISO-standard 25178-2 [124]:

The areal material ratio curve (the s-shaped black line on the picture to the right-hand side of Figure 34) is obtained by plotting the material ratio (from 0 to 100 %) which is intersecting with a x-y-plane at a certain height z versus the according z-values. Based on this, the areal surface roughness parameter can be calculated. At first, the equivalent straight line must be found (red line on the picture to the right-hand side of Figure 34). This is the secant over a material ratio of 40% with the smallest gradient. The difference between the z-values of the intersection of the equivalent straight line with the vertical lines at 0 % and 10 % material ratio determines the core height $S_k$. The material ratio related to the intersection at 0 % is defined as $Smr_1$ and the ratio related to the intersection at 100 % as $Smr_2$. $Smr_1$, therefore, determines the material ratio, which is protruding from the core roughness while $Smr_2$ is indicating the material ratio of valleys below the core roughness. Based on the horizontal line between the intersection point of the equivalent straight line and the material ratio curve, a right-angled triangle is constructed (hatched yellow triangles in Figure 34). This triangle has the same area as the area between the graph, the horizontal $Smr_1$ line for $Spk$ ($Smr_2$ line for $Sv_k$) and the vertical line at 0% for $Spk$ (100% for $Sv_k$). The lengths of the vertical cathetus in these triangles define $Spk$, the reduced peak height, and $Sv_k$, the reduced dale height. These parameters are a measure of the average height of the protruding peaks above the core roughness ($Spk$) and the dales below the core roughness ($Sv_k$). The averaging process, due to the calculation of these parameters, reduces the influence of outliers. The z-value of the highest peak found in the material ratio curve is referred to as $Sp$ and the lowest value as $Sv$.

Out of the set of areal surface roughness parameters described in this standard, two can be useful to describe the blistered surface, namely:

- $Spk$: the reduced peak height
- $Smr_1$: the material ratio which separates the protruding peaks from the core roughness profile

$Spk$ is preferred to $Sp$ since $Sp$ can be determined by a single outlier. $Spk$, instead, is the average height of the peaks above the roughness core profile and therefore less sensitive to the influence of
outliers than Sp. Smr1 represents the percentage of material above the roughness core profile and can be taken as an indicator of how much of the investigated area is related to blisters [124].

Median filters are suggested in the software for noise reduction, for which a median 15x15 full filter was chosen. These non-linear filters use a window of a certain size (in this case 15x15 Pixel) and investigate the height values. If the value in the centre of this window differs too much from the median value of the window, it is replaced by this median value. The threshold for the maximum difference between the centre value and the median, hereby, depends on the standard deviation of the values within the window. The detailed algorithm is not revealed by the software. Median filters are superior to mean-filters for noise reduction since the image blurring is less for the median filter [125]. Median filters are efficient filters for the removal of speckle noise and are often presented as reference when new filtering methods are proposed [126]–[128]. Since the procedure described above was kept consistent for all the measured samples, the values can be used for a qualitative comparison of the influence of the varied injection moulding parameters on blister creation.

Figure 35 shows the correlation between degree of blistering and the parameters Spk and Smr1. Picture a) shows a blister-free surface with low values for both Spk and Smr1. Picture b) shows a badly blistered surface, which is represented by high values for both roughness parameters. Indicated by the red colour, high blisters can be identified. In this Picture, the blisters are covering a large proportion of the surface area (high Smr1) and are protruding significantly from the unblistered area (high Spk). In Picture c) and d) some spread blisters can be found. The similar Spk values indicate that the average height of the blisters is almost identical for both samples. In part d), however, the higher Smr1 value indicates a larger detached area, which is represented by the higher share of red areas in this picture.
Ten repeated measurements on the same part showed a standard deviation of 2.4 µm for the $Spk$ value and 0.9% for $Smr1$ for this measurement procedure.

### 5.1.5 Results

**CT-scans**

The CT-scans of the blister free specimens did not show any signs of delamination of the film insert from the substrate. Furthermore, its homogeneous appearance indicates that the gaps between the single fibres of the non-woven support layer have been filled with the PP-melt of the substrate since no signs of trapped air in the interface region could be found (Figure 36).

![Figure 36: CT-scan of a blister free part](image)

In the blistered parts, it was found that the blistering occurred due to a delamination between the membrane and the support layer (Figure 37). This indicates that the weak spot in this layered specimen is the interface between the membrane layer and the support layer.

![Figure 37: CT-scan of blistered specimen](image)

Even though it was found that single fibres stuck to the membrane and got pulled out of the substrate (see Figure 38), the CT-scans showed good filling of the non-woven support layer for the blistered parts, too.
The filling of the non-woven structure is important for good adhesion between the film insert and the substrate. When this non-woven layer is filled properly, there are many PP fibres which are surrounded by the melt. This allows for a good mechanical interlocking between the film insert and the substrate, which is stronger than the adhesion between the support layer and the membrane.

Figure 38: Pulled out fibre at a blister
**In-process-monitoring**

The IPM videos revealed no visible differences in the filling phase of the moulding cycle between the blistered and the unblistered parts (see Figure 39a & b)). It can therefore be expected that no delamination occurs due to the mechanical stresses (especially shear stresses can be expected) created due to the melt flow. The moulding parameters for the two parts can be found in Table 12.

<table>
<thead>
<tr>
<th>Part ID</th>
<th>Mould Temperature</th>
<th>Barrel Temperature</th>
<th>Injection Speed</th>
<th>Packing Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 6 P1 (left hand side)</td>
<td>40</td>
<td>270</td>
<td>300</td>
<td>126</td>
</tr>
<tr>
<td>Run 8 P1 (right hand side)</td>
<td>40</td>
<td>200</td>
<td>300</td>
<td>72</td>
</tr>
</tbody>
</table>

During the cooling phase, differences could be observed. For parts, which showed a high degree of blistering, blister creation and growth could be seen. This was visible by bright spots that appeared all over the membrane when the cooling phase started as it can be seen in Figure 39 c). The unblistered part in the picture on the left-hand side shows a way more homogeneous bright area at the left side of the sapphire window than the blistered one (picture on the right-hand side in Figure 39 c)).

The moment when the part shrinks away from the mould can be observed by a change in brightness in the area around the membrane in the high-speed-videos. While that happens quite homogenously for the parts without blisters, the shrinkage front is way more irregular for parts with a high degree of blistering (see Figure 39d). In the picture on the left-hand side, an almost continuous bright front can be detected while on the picture on the right-hand side this front is interrupted under the membrane area where inhomogeneous shrinkage occurs. The shrinkage in the inhomogeneous case starts at different positions close to each other and is visible as a cluster of bright spots.

The reason for the direction of the shrinkage front from the left side of the sapphire window towards the right can be found in the mould design. The gate of the part can be found on the right-hand side. This leads to a difference in cooling time due to the filling behaviour between the left side of the part and the right side. The material which enters in the beginning of the filling phase will end up at the end of the part once the frozen layer is established while the material close to the gate can enter the cavity even during the packing phase, and therefore the cooling time for the material on the left-hand side is longer than that for the material at the right-hand side. Therefore, the detachment of the part due to shrinkage shows this front, which moves from the left-hand side to the right.
The observed behaviour and the fact that blisters were found to be a delamination of the membrane layer indicate that the blister creation happens due to differences in the shrinkage behaviour of the membrane and the substrate.

**Comparison IPM vs. Simulation filling phase**

For a validation of the simulation results, the filling phase seen in the IPM videos can be compared to the one observed in the virtual experiments. It was found that the shape of the flow front in the observed area in the videos is in good accordance to the flow front behaviour in the simulations (see Figure 40). The black ring in the pictures on the left-hand side of Figure 40 indicates the area which was observed by the high-speed camera. In the simulated filling behaviour, it appears that the flow front hesitates under the film insert. This is due to a smaller cross-section in this area compared to the uncovered area. This hesitation causes the higher curvature of the flow front at the edges of the film insert, which can also be seen in the pictures with the IPM-video overlay on the right-hand side in Figure 40. This leads to the conclusion that the flow behaviour found in the simulations is similar to that in reality. The white lines in the pictures on the right-hand side indicate the flow front in the
video. While it is clearly visible in the uncovered area next to the film insert, as shown in Figure 39, the dashed white lines indicate the flow front under the film insert estimated from the change in brightness visible in the video (see Figure 40 and Figure 41). This white line was inserted manually to improve the visibility of the flow front under the membrane. The flow hesitation effect seems to be less pronounced, and at the same time the flow front is not always as uniform under the film insert as in the simulation. In the uncovered area, however, the observed flow front is in good agreement with the flow front found in the simulation. This behaviour is most likely caused by the non-woven support structure and the ongoing changes in the cross-section of the flow channel under the film insert due to variations in the number of fibre layers in the non-woven support.

Figure 41 illustrates the degree of filling over time for Run 8 P1. Picture a) shows, for both the IPM sequence and the simulation, the point when the melt reaches the observation at the sapphire window. That point is reached in the simulation after 0.0194 s and is chosen as a zero point for this comparison. Around 5 ms later, a bit less than half of the observation area is covered in the real and the virtual experiment (Figure 41 b)). Another 5 ms later, the observation area is almost entirely covered (Figure 41 c). The point where the observation area outside of the film insert area is covered is reached after another 2.6 ms (Figure 41d). While comparing the steps c) and d) and the time interval between them shows a good reproduction of the real experiment in the simulation, it is difficult for the other steps to find the frame in the video that corresponds to the simulation since the biggest part of the flow front is covered in a) and d). Therefore, the difference between the filling time for the presented section between the simulation and the video, which was found to be 1.4 ms (simulated time was 0.0129 s, time calculated from the video 0.0115 s) is small enough (relative error of 1.2%) to consider the simulation results a good representation of the filling phase of the real experiment.
Figure 40: Simulated filling behaviour of Run 6 (left hand side), overlay of experimental video (right hand side)
Figure 41: Degree of filling at certain times. Comparison between IPM-video (sequence on top) and Simulation (sequence at the bottom) for run 8 part 1.
5.1.6 DOE Evaluation

In injection moulding, most of the parameters influencing the dimensional quality of the final part show a linear behaviour and are related to speed, pressure, time and temperature. Sometimes non-linear behaviour can be found for the influence of e.g. cooling time or packing pressure where particular responses might plateau off. Furthermore, it is expectable that in an injection moulding process no interactions higher than two factor interactions will occur. In addition, these interactions are usually mild and overpowered by the main effects of the factors [129]. Because the reason for the creation of blisters during film insert moulding is unknown, three levels were chosen for $T_{\text{barrel}}$, $v_i$, and $P_{\text{pack}}$. This choice should avoid that effects of a higher order are completely ignored. For $T_{\text{mould}}$, two levels were chosen to reduce the number of experiments since linear behaviour was found for warpage, crystallinity and crystal size in the film insert moulding with PP as overmoulding material in [64]. Therefore, the effect of the mould temperature on shrinkage related issues is expected to be linear in film insert moulding.

As described in section 5.1.4, two areal surface roughness parameters $Spk$ and $Smr1$ were investigated for the evaluation of the blistered film surface of the moulded parts and are used as input for the DoE.

$Smr1$

In Figure 42, the main effect plots for $Smr1$ are presented. While the symbols in these plots represent the mean value of all the observations at the according level of the factor, the standard deviation of the mean is represented by the error bars. $T_{\text{barrel}}$ has the strongest influence on $Smr1$, which decreases steeply when $T_{\text{barrel}}$ is increased between 200 °C and 235 °C followed by a slighter decrease between 235 °C and 270 °C. The effect of $T_{\text{mould}}$ is way weaker, whereas the effect of $v_i$ appears to be statistically not significant. For $P_{\text{pack}}$, a statistically significant influence can be found between the middle level and the high level of the factor.

These findings can be backed up by an analysis of variance (ANOVA) conducted on the mean values using the statistical Software “Minitab 17”. The significance level $\alpha$ was chosen as 0.05 which means that a P-value smaller than $\alpha$ would lead to a rejection of the hypothesis that there is no significant difference in the compared values. [130].

The only two factor interaction influencing $Smr1$ was found to be the interaction between $T_{\text{mould}}$ and $T_{\text{barrel}}$. The according interaction plot is shown in Figure 43.
Figure 42: Main Effects of chosen parameters on Smr1

Figure 43: Interaction of $T_{mould}/T_{barrel}$ on Smr1
This plot shows a strong effect of an increase in $T_{\text{barrel}}$ on $Smr1$ at low $T_{\text{mould}}$, while there is a way weaker effect at the high level of $T_{\text{mould}}$. The resulting multiple linear regression equation for $Smr1$ in % is

$$Smr1\% = 171.5 - 1.280 \times x_1 - 0.931 \times x_2 - 0.0369 \times x_3 + 0.001237 \times x_2^2 + 0.00513 \times x_1 \times x_2$$ \hspace{1cm} \text{Eq. 5-13}$$

where $x_1$ is $T_{\text{mould}}$ (in °C), $x_2$ is $T_{\text{barrel}}$ (°C), and $x_3$ is $P_{\text{pack}}$ (bar). This regression equation explains 63.23% of the variation in the observations (adjusted $R^2$ value). This value is rather low and the model is therefore not adequately representing the influence of the factors. The intention of using a quadratic regression model in this investigation, however, is to identify significant, non-linear effects. Such an effect can be found for $T_{\text{barrel}}$, which is indicated by the quadratic term in the regression model. This approach can be used to identify factors which would have to be investigated further (e.g. by a higher number of levels) to obtain a more precise regression model that could describe the underlying effects better.

The influence of the factors (according to the MS-value) in descending order is:

- $T_{\text{barrel}}$ (MS= 379.83), Interaction of $T_{\text{mould}}$ and $T_{\text{barrel}}$ (MS=116.06), $P_{\text{pack}}$ (MS= 35.7), $T_{\text{mould}}$ (MS=30.1) and the quadratic term of $T_{\text{barrel}}$ (MS=27.5).

According to the results, the processing temperatures are the main influence on the amount of material protruding from the core roughness ($Smr1$-value). A higher barrel temperature decreases the viscosity of thermoplastic materials, which leads to a better filling behaviour, especially of the small gaps between the fibres of the non-woven material. A higher mould temperature can have the same effect. This can lead to a more uniform cooling and shrinkage behaviour and consequently to less blister creation. Furthermore, an increase in $T_{\text{mould}}$ reduces the thickness of the frozen layer and can improve the intimacy between the membrane and injected material, too.

The significant interaction of $T_{\text{mould}}$ and $T_{\text{barrel}}$ indicates that the effect of the barrel temperature is less influential at high mould temperatures. This can be explained by the time it takes to cool the injected melt. At higher $T_{\text{mould}}$, the polymer will take longer to cool and freeze. The cooling rate influences the crystallinity of the material and by that the shrinkage. The interaction could be explained by a higher shrinkage of the injected material and a consequent increase in the difference in shrinkage behaviour of the PET layer of the membrane and the PP of the substrate at the high level of $T_{\text{mould}}$. As described in chapter 2.3.2, an increase of $T_{\text{barrel}}$ reduces the thickness of the skin and the shear layer. The core layer thickness, where spherulitic crystals are created, is increased which can lead to a higher amount of ordered structures and therefore to a higher shrinkage at the combination of the high levels of $T_{\text{mould}}$ and $T_{\text{barrel}}$.

Another possible explanation for the interaction of the temperatures is the relaxation of residual stresses in the fibres of the non-woven support layer. Relaxation processes are accelerated at higher temperatures. If the temperatures are high enough, relaxation of the tensile stresses in the fibre material could set in, which would lead to a contraction of the fibres and therefore to a difference in
shrinkage between the PET-layer and the non-woven support. This could lead to detachment of the PET-membrane from the support.

The main effect of $P_{\text{pack}}$ shows an improvement in part quality (reduction of $Smr1$) when the packing pressure is increased from the medium to the high level, whereas the part quality is nearly constant between the low and the medium level of this factor. This indicates that the two lower levels are chosen too low and do not contribute to packing. They are high enough to prevent a backflow of the melt, but only the high level seems to improve the packing of the part. In case of backflow, a significant decrease in the $Smr1$ value would be expected between the low and the medium level due to higher shrinkage of the moulded part. If the part is properly packed, the volumetric shrinkage of the substrate material will be less and blister creation will be reduced. On top of that packing can improve the contact between the part and the mould surface and lead to a better heat transfer between the part and the mould and consequently to a more uniform cooling behaviour.

![Residual Plots for Smr1](image)

*Figure 44: Residual analysis for regression model of Smr1*

Figure 44 shows the residual plots for the regression equation (Eq. 5-13). The normal probability plot and the histogram indicate a normal distribution of the residuals. The slight deviations from the linear behaviour in the normal probability plot and the bell shape of a Gaussian normal distribution can be explained by the relatively low sample number. This could be improved by running more replicates of the chosen design.

In the plot for the residuals versus the running order no trends can be found. The plot of residuals versus the fitted values is structureless. These plots therefore indicate no violation of the independence or constant variance assumption, which is a prerequisite for the use of the ANOVA.
Some large residuals can be found in those plots, e.g. for run 10 and 46, in the residual versus the observation order plot. These large residuals can indicate an outlier, but in this case they are not extreme and might not be considered as large residuals in an experiment with a bigger sample size [116].

Investigating the within run variability by taking the natural logarithm of the variance of the single runs as an observation value for the DoE, indicates the influence of the process parameters on the repeatability of the results. Even though the regression models for these investigations usually explain only a small part of the variability, they can be used to get an idea about the trends which can be found [116].

Figure 45 shows the main effects on the repeatability of the process in terms of Smr1. The tendency shows that the variability of Smr1 can be expected to be lower at low $T_{\text{mould}}$ and high $T_{\text{barrel}}$. $P_{\text{pack}}$ and $v_i$ are without statistical significance at an $\alpha$-level of 5%. The residual plot did not show any conspicuousness. A statistically significant interaction was found for $T_{\text{mould}}$ and $T_{\text{barrel}}$, which is shown in Figure 46.

Figure 45: Main effect plots for the within run variability for Smr1

Figure 46: Interaction for the within run variability of Smr1
The low R²-adjusted value of 12.43 % found for the underlying regression model states that the contribution of a change in the investigated process conditions on the change of the within run variability is rather small.

**Spk**

The same approach as for Smr1 was chosen to investigate the influences of the chosen moulding parameters on the reduced peak height (Spk) of the blisters. The main effect plots can be found in Figure 47. The trends in the main effect plots are similar to those found for Smr1. This was expectable since higher blisters also lead to a larger share of the surface above the core roughness. According to ANOVA for α=0.05, the only nonsignificant main effect is, as it was found for Smr1 already, vi. In contrast to Smr1, Spk is influenced by three two factor interactions. One of these is the same as for Smr1, namely the Tmould*Tbarrel interaction. The second interaction, which is found to be significant, is the interaction between Tbarrel and Ppack and the third is the interaction between Tmould and vi.

![Figure 47: Main Effects of the parameters on Spk](image-url)
The increase in the reduced peak height when changing from the low mould temperature to the high mould temperature at the high level of the barrel temperature appears to be more pronounced than for the material ratio before (see Figure 48). This indicates that the before mentioned shrinkage difference due to a higher crystallization at the high level of both temperature levels might influence blister creation. A final statement on this could be given when the crystallinity of the PP for those parts would be investigated.

The second interaction, which appears to be significant (see Figure 49), is the one between $T_{\text{barrel}}$ and $P_{\text{pack}}$. This is due to the packing, which apparently reaches a plateau at the high level of $P_{\text{pack}}$ and the medium level of $T_{\text{barrel}}$. Furthermore, the packing is equally good for all the chosen levels of packing pressure at the high barrel temperature. This can be caused by the low viscosity and the extended gate freeze off time at the high level of $T_{\text{barrel}}$. 

![Figure 48: Interaction of Mould Temperature and Barrel Temperature on Spk](image)

![Figure 49: Interaction of Barrel Temperature and Packing Pressure on Spk](image)

![Figure 50: Interaction of injection speed and mould temperature](image)
The third interaction affecting \( Spk \) is the one between \( T_{mould} \) and \( v_i \). At a high mould temperature, an increase of injection speed causes no changes in \( Spk \) or even a slight increase, while at low \( T_{mould} \) a decrease of \( Spk \) with increasing \( v_i \) can be found. This effect might be caused by a higher number of flow induced nuclei due to the higher orientation at higher injection speeds in combination with a lower cooling rate at the high level of \( T_{mould} \).

A lower viscosity requires less pressure to keep up some flow through an identical channel, and therefore a lower \( P_{pack} \) can be sufficient for packing. The extended gate freeze off time at a higher barrel temperature enables material to flow into the cavity for a longer time and therefore compensates better for the shrinkage of the cooling part.

\[
Spk = 441.7 - 2.564 \times x_1 - 2.299 \times x_2 - 0.937 \times x_3 - 0.1039 \times x_4 + 0.00282 \times x_2^2 \\
+ 0.00805 \times x_1 \times x_2 + 0.001881 \times x_1 x_4 + 0.00364 \times x_2 x_3
\]  

Eq. 5-14

Eq. 5-14 is the regression Equation for \( Spk \) in \( \mu m \). This equation explains 68.13\% of the variation in the observations according to the adjusted \( R^2 \) value. In this equation \( x_4 \), is the injection speed. The regression model contains \( x_4 \) for hierarchy reasons due to the significant interaction between \( T_{mould} \) and \( v_i \) (P-value for \( v_i \): 27.7\%, for interaction \( T_{mould}/v_i \): 4.1\%).

The strongest influences can be found by the processing temperatures and their interaction followed by the interaction between \( P_{pack} \) and \( T_{barrel} \), the main effect of \( P_{pack} \), the quadratic term for \( T_{barrel} \) and the least influence can be found by the interaction of \( T_{mould} \) and \( v_i \) and the main effect of \( v_i \). The MS values can be found in Table 13:

<table>
<thead>
<tr>
<th>Factor</th>
<th>( T_{barrel} )</th>
<th>( T_{mould} )</th>
<th>( T_{barrel} \times T_{mould} )</th>
<th>( T_{barrel} \times P_{pack} )</th>
<th>( P_{pack} )</th>
<th>( T_{barrel} )</th>
<th>( T_{mould} \times v_i )</th>
<th>( v_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS-value</td>
<td>1957.8</td>
<td>476</td>
<td>285.5</td>
<td>283.4</td>
<td>187.9</td>
<td>143.4</td>
<td>127.3</td>
<td>34.8</td>
</tr>
</tbody>
</table>
Both the histogram and the normal probability plot of the residuals are slightly skewed to lower values. This indicates a violation of the normality assumption, which can be problematic when the F-test is used. In this case, though, the small sample size can explain the moderate deviation from a normal distribution and is therefore not problematic.

The residuals versus the fitted values plot does not show any structure and the residuals versus the observation order plot does not indicate any trends. Four large residual values were found for run 9, 40, 46 and 52.

Investigating the within run variability for Spk, showed an increase in repeatability for an increase in both investigated temperatures (see Figure 52). Other influences could not be found. The underlying model accounts for a bit more of the variability than that found for Smr1. The obtained R²-adjusted value was 19.69 %. The model, therefore, only explains around one fifth of the found within run variability.
5.1.7 Simulation results

Investigation of the injection pressure

A further comparison between the simulation and the experiments can be done by the maximum injection pressure. In the experiments, this injection pressure was recorded by a load cell at the end of the injection plunger. A conversion factor which considers the diameter of the injection plunger can be used to calculate the injection pressure from the output voltage of the load cell. The comparison of the measured maximum injection pressure and the simulated maximum injection pressure in terms of the difference between those two can be found in Figure 53.
Due to problems with the acquisition system, the pressures could not be measured for each part of the run in some cases. Therefore, the number of measurements is indicated by the black squares. Error-bars are used to indicate the standard deviation when more than one measurement was taken, and the difference was calculated as the difference between the average value of the maximum injection pressure found in that run and the maximum injection pressure obtained by the simulation. It was expected that the simulation deviates from the real value for several reasons. These reasons are:

- The simulation model only takes the flow path inside the mould into account. The fluidic resistance of the barrel is, therefore, neglected in the simulation [43].
- The model of the membrane is expected to lead to a lower fluidic resistance in the simulation due to the smooth surface in this model. In reality, it is expected that the non-woven support layer leads to flow disturbance and a higher fluidic resistance.
- The model of the venting channel can over- or underestimate the venting behaviour of the real mould, which influences the accuracy of the pressure calculation [43].

**Figure 53: Difference between the maximum injection pressures obtained from the experiments and the simulations**

![Graph showing the difference between measurement-simulation and number of measurements](image)
- The parameter $D_3$ for pressure dependence in the Cross-WLF-model (see section 2.3.2, Eq. 2-12) is set to zero in the material model in the AMSI2016 database. If the pressure was considered, an increase in pressure would lead to an increase in viscosity. Therefore, the simulation underestimates the injection pressure when the pressure dependence is neglected.
- The compressibility and the influence of crystallinity on the viscosity (see section 2.3.2., Eq. 2-29) are neglected in the simulation.

![Figure 54: Relative Deviation of the maximum injection pressure between measured and simulated values.](image)

Nevertheless, the deviations found are rather big, especially for the runs number 6, 9, 10, 15, 19, 22, 23, 41, 42, 47 and 53. These runs show relative deviations of up to 248 % (run 15) of the simulated values (see Figure 54). These high deviations indicate that the reason for the deviations does not only originate from the simulation. It is more likely that the switch-over for the runs with the large differences between the measured and the simulated value was too late. The switch over point in this kind of investigation is a rather critical point. First of all, the volume of the part is very small (116.85 mm³), as for most micro parts. This results in the fact that the difference between a switchover at 98 % of the part filled and one which happens when the part is already filled is a volume
of 2.34 mm³. This corresponds to a difference of 120 µm plunger stroke in the injection moulding machine utilized for these experiments. The rather large error bars for some of the runs in Figure 53 indicate that the repeatability of the injection process in these experiments could be problematic. This can be caused by several factors:

- The PP used for overmoulding.

Quite large deviations between the filling degrees were found, when completing the first short shot experiments with the used PP. This could be reduced by using the maximum back pressure for the plastification of the machine of 100 bar. This equals the lower level of back pressure recommended in the processing guide. The filling repeatability found for the part-weight of 10 parts moulded with $T_{mould} = 40 ^\circ C$, $T_{melt} = 200 ^\circ C$ and $v_i = 300$ mm/s without a packing phase and without the film insert was found to be 93.9 mg with a standard deviation of 4.2 mg. Using the material's density of 905 kg/m³ at 23 °C, the deviation of the weight corresponds to a volumetric deviation of 4.6 mm³. This equals 4 % of the parts volume and explains that both the over- and underestimation of the maximum injection pressure by the simulation can be found.

Another source for deviations in the filling process is the manual preparation and insertion of the film insert. The double-sided tape used to fixate the film insert was cut by hand and could, therefore, vary in width and length. Even though this tape was used outside of the cavity, its size could influence the venting behaviour and therefore the filling behaviour. The film insert was mounted by hand. Even though the recess was used for alignment, other factors like the tension in the film insert might have varied due to the manual insertion. This could be another reason for variations of the filling pressure.

A switch over which is too late leads to an instant increase in the maximum packing pressure. If the machine continues to inject with the high velocity, which is set for the filling phase, when the part is completely filled, the material inside of the cavity is being extremely compressed, which leads to a steep increase in the injection pressure.

A pronounced correlation could be found for the injection moulding parameter used in the runs showing the high maximum injection pressure. Seven out of the eleven runs, which showed problems with a late switch over, were using the combination of the high level of mould and the high level of barrel temperature. This can be another reason for the non-linear behaviour found in the DoE-analysis for the barrel temperature and the pronounced interaction of these two parameters.

**Average Volumetric Shrinkage under film insert**

The results found in this investigation indicate that the shrinkage of the overmoulding material is one of the reasons for the blister formation. Therefore, the average volumetric shrinkage under the film insert was investigated by means of the simulation results. The average volumetric shrinkage is the volumetric shrinkage at a chosen position of the part divided by the part's thickness at this position. For the investigation, a path plot of several positions in the AOI in Figure 32 under the membrane was created (see Figure 55).
The average of the shrinkage values at the 16 positions shown in Figure 55 was calculated and used for the evaluation in the DoE. The results of the main effects can be found in Figure 56.

In accordance to the findings in the experimental work, the injection speed is found to be statistically insignificant. The order of the influence of the parameters, however, is changed for the simulation results. Here, the influence of $P_{\text{pack}}$ is found to be the strongest followed by $T_{\text{mould}}$, $T_{\text{barrel}}$ and the interaction between $P_{\text{pack}}$ and $T_{\text{barrel}}$ (see Figure 57).
These differences could indicate that the shrinkage of the overmoulding material is not the only reason for the blister creation.

Other effects, which are mainly caused by high temperatures and not considered in the simulation, might contribute to the blister creation, too. One of these effects can be the, already mentioned, stress relaxation in the fibres of the non-woven support layer, which could lead to a contraction of the fibres and therefore a delamination between the PET-layer and the substrate.

Especially at low cooling rates the crystallization effects could increase the shrinkage, which is not considered in the simulation. Furthermore, in this part the highest shear rates can be found at the gate. High shear rates can cause an elevation of the no-flow temperature in semi-crystalline materials. This can lead to a faster gate-freeze-off than calculated by the software. When the gate freezes off faster, the time in which $P_{\text{pack}}$ can efficiently maintain a flow into the cavity is reduced and therefore less material will be available to compensate for the part’s shrinkage. This can lead to an overestimation of the influence of the packing pressure in the simulation.

Figure 56: Main effects plot for simulated average shrinkage
Furthermore, the effect of pressure on the materials viscosity is neglected. The increase in viscosity with higher pressure can, therefore, reduce the influence of an increase in packing pressure.

The problems concerning a correct switch-over point might cover the effect of packing pressure in the experimental results, especially at the high-level combination of \( T_{\text{barrel}} \) and \( T_{\text{mould}} \). Since the pressure rises at the end of the filling phase to a very high level, the parts for these settings might show a high degree of packing before the actual packing phase begins. This could lead to an underestimating of the influence of the packing pressure in some of the experimental runs.

The influence of the temperatures on the shrinkage under the film might be underestimated because of the idealized model of the support layer. At increased \( T_{\text{barrel}} \), the viscosity is lower, which could lead to a better filling of the microstructures of the non-woven support layer (see section 2.3.2). This can reduce air gaps in this layer and increase the contact area for the heat exchange, which could lead to more homogenous cooling conditions and a higher cooling rate, which would reduce crystallization and therefore the shrinkage. At the high level of \( T_{\text{mould}} \), the frozen layer is expected to be thinner, which could also lead to a better filling of the non-woven layer.

Figure 57: Interaction of barrel temperature and packing pressure on the simulated average shrinkage
The residual plots for the regression model of the simulation are showing only one outlier and are otherwise indicating a perfectly normal distribution of the residuals. This was expectable because simulations are dealing with perfect processing conditions. External influences, which can influence the outcome, like the manual insertion of the film insert or environmental influences of the process (e.g. changes in room temperature, etc.) are not taking into consideration in simulations.

5.2 Container Moulding

The presented mould design for the fuel cell container was validated by flow simulations prior to the manufacturing of the mould. Moulding experiments revealed problems with the implemented vacuum film insert fixation system. These problems have been solved by changes in the design of the interface between the vacuum channel and the membrane. Finally, film insert moulding could be conducted successfully. These steps are presented in this section.

5.2.1 Simulation

Injection moulding process simulations have been executed for the container mould. These simulations aimed at the validation of the filling behaviour of the sprue, runner, gate and cavity structure before the mould was manufactured.
For these simulations, the 2014 version of Autodesk Moldflow was used. In this version, the overmoulding feature was not implemented yet. The film insert was modelled as a 200 µm thick PP part insert (material: generic PP from the AMSI database). The difference between the part insert and the film insert model, which was described in chapter 5.1.2, is that the part insert is meshed with a 3D-tetrahedral mesh, and the thermal mass of the insert part is taken into consideration. In this simulation, only the part was modelled. The mould temperature is, therefore, assumed to be homogeneously distributed. This approach will not lead to precise simulation results but is sufficient to get information on the filling behaviour (including the fill pattern, the injection pressures, the fill time, etc.) and the occurrence and the order of magnitude of phenomena like e.g. weld line creation and warpage. As in the simulation of the material test part, a multi-scale mesh was used. While larger edge lengths were chosen for the elements at the sprue and the runner, a finer mesh was chosen for the container and an even finer one at the interface between the membrane and the overmoulding material (see Figure 59).

![Figure 59: Different mesh sizes in the multiscale mesh](image)

A model of the machine, which was intended to be employed (Engel ES 80/25 HL-Victory), was implemented and 3 venting channels were set to model the venting at the primary parting line.

A full factorial DOE-analysis was conducted to investigate the part filling behaviour, get an estimation of the part warpage and the remelting areas on the film insert. The investigated parameters were the mould and the melt temperature, the injection speed and the packing pressure. For each parameter, two levels were chosen. The according values can be found in Table 14.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low level</th>
<th>High level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mould temperature in °C</td>
<td>20</td>
<td>60</td>
</tr>
<tr>
<td>Melt temperature in °C</td>
<td>190</td>
<td>270</td>
</tr>
<tr>
<td>Injection speed in mm/s</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>Packing Pressure in % of maximum filling pressure</td>
<td>40</td>
<td>70</td>
</tr>
</tbody>
</table>
The mould temperature, the melt temperature and the packing pressure were chosen based on the processing recommendations of the material supplier [113], the injection speed was chosen to achieve filling times below one second.

**Fill analysis**

The fill analysis showed that the filling of the part is possible; the maximum injection pressures were found between 16.34 MPa and 33.62 MPa. These pressures can be realized by the chosen injection moulding machine [45].

The filling times were between 0.33 s and 0.55 s. These are acceptable values for the prototype production. The filling analysis for some runs showed problems with the filling of one of the edges at the sprue puller, and were considered as short shot by the software. The filling times for these runs were determined from the time of the velocity controlled filling phase to the switch-over to the pressure controlled packing phase, which was set at 99 % of the part volume filled and therefore independent of the filling of the sprue and the runner. The tetrahedral elements of the runner and the sprue were assigned a "cold runner" in the mesh and therefore the filling of these sections is not considered for the switch-over and warpage calculation.

![Image](image_url)

**Figure 60: Unfilled section in the sprue puller (Run 3)**

This filling problem of the sprue, however, is not expected to be a problem for the mould but rather a problem in the simulation model. This is due to several reasons:

- The part is symmetrical and the mould temperature is homogenous in this type of simulation. An asymmetric effect in the filling behaviour is, therefore, improbable.
- The pressures in the unfilled section reach the same values as in the filled section with the same geometry on the other side of the sprue puller at the same melt temperature, which is why the filling of this section can be expected.
- The air trap analysis does not show trapped air in this section. The software indicates the run as a short shot.
Since no reasons for a short shot or improper filling of this section could be found, it is expected to be a problem of the simulation model or the mesh. Furthermore, this problem occurs in the sprue puller, which is an uncritical feature for an effect of this size. Therefore, it could be expected that the mould design is functional.

This problem occurred for the DoE-runs 3, 7, 10, 11, 12 and 16. A table with the according settings can be found in the appendix.

In Figure 62, a typical filling pattern is shown. At the bottom of the container a circular pattern starting from the gate in the centre of the part can be found (pictures a) and b)). When the melt reaches the sidewalls, a racetrack effect occurs at the corners of the container. Since the corners are not covered by the membrane, the cross-section of the flow channel is larger in this area, which leads to a higher flow rate (picture c)). In picture d) the two melt fronts, which emerged when the melt flew around the pin for the CO$_2$ venting hole, reunite. This can lead to the creation of a weldline, which can cause a reduction in the mechanical properties such as yield strength in this section of the part. The influence of the race track effect is still visible in the section where a uniform cross-section can be found (pictures f) and g)). Finally, the part is entirely filled (picture h)).
Figure 62: Filling sequence of the container
Re-melted areas

In film insert moulding, the re-melted areas are of special interest for the adhesion between the membrane and the overmoulded part (see section 2.2.3 and 3.2.2). Examples of the different fractions of the re-melted area are shown in Figure 63. It was found that the film insert at the bottom of the container is re-melted for each of the chosen process parameters combination. The fraction of the area on the side walls, however, varies with the process conditions and was found to be between around 20 % and 100 %. The software output for this analysis is only graphical; the presented values are based on estimated area fractions according to the pictures. In the picture of Run 5 in Figure 63, the flow hesitation around the pin for the CO₂-venting hole leads to differences in the re-melted area on the sides of the container with and without this feature. Due to the flow hesitation, the melt is slightly colder when it reaches the section below the pin and is not able to re-melt the surface of the film insert anymore. Therefore, the re-melted area on the sides without the feature is slightly bigger.

![Figure 63: Re-melted area (From left to right): ~20 % of sidewall area (run 1), ~40 % (run 3), ~60% (run 5) and 100% (run 16)](image)

The estimated percentages were used as output values for the DoE analysis. These analyses showed an increase in the re-melted area with an increase in the melt temperature, which was expected. Another expectable effect was found in the increasing re-melted area fraction with an increasing mould temperature. This effect is smaller in total numbers. The reason for this can be found in the smaller change in temperature between the low and the high level. The effect per degree Celsius of the mould temperature is bigger than that of the melt temperature.

A surprising effect can be found in the slight decrease of the re-melted area with an increasing injection speed. Typically, it would be expected that higher injection speeds lead to a bigger re-melted area for two reasons:

- A higher injection speed shortens the filling time, which leads to a higher temperature at the flow front at a certain position in the mould.
- Higher injection speeds cause higher shear rates in the material. This leads to shear heating of the material, which should increase the melt temperature.

The effect of the injection speed, however, is the weakest of the effects found significant for the regression model with an α –level of 15 %. On top of that, the used values are based on estimates, and slight deviations from the actual value must be expected. And last but not least, the sample size with sixteen runs is not big enough to get a statistically reliable regression model. The tendencies
found with this method for the strong main effects, however, can be expected to be found in real injection moulding experiments, too.

**Warpage**

Warpage can be expected to be one of the biggest issues in this mould-design. For box shaped injection moulded parts warpage of the sidewalls towards the inside of the container is a well-known phenomenon (see Figure 64) [131]. In addition to the so-called corner or box effect, the film insert causes inhomogeneous cooling conditions, which can create additional warpage.

![Figure 64: Warpage in the container; left hand side box effect, right hand side: warpage in direction of the part height (y-direction). Warpage magnified by a factor of five in both pictures](image)

The path plot function of AMSI was used to investigate the warpage along the edges at the interface between the container and the fuel cell since this is the only dimension of the container with a geometrical specification which is expected to be affected from warpage and is important for the assembly with the fuel cell. For this investigation, several points along the edges in z-direction have been investigated concerning the warpage in x-direction and vice versa. The warpage was characterized by the deviation of the minimum point to point distance between the two opposing sides from the target value. Therefore, the measurement points along the container to fuel cell interface edge where chosen as shown in Figure 65.
In Figure 66, the main trends for the influence of the process parameters on warpage found by the simulation are presented. The part design was kept symmetric to the greatest possible extent; therefore, the tendencies are in principal the same for warpage in x- and y-direction. According to the simulation, the warpage will cause a deviation of between 43 µm and 144 µm. In 15 out of 16 runs, the warpage was found to be slightly larger (between 0.1 µm and 1.6 µm) for the z-direction than for the x-direction. This effect is expected to be caused by the distortion of the symmetry of the part by the venting holes.

Figure 65: Measurement points for part warpage; left hand side: warpage in z-direction, right hand side: warpage in x-direction
In general warpage is the result of differences in shrinkage during cooling and can have several reasons such as differential cooling, the polymer orientation, differences in part thickness, pressure distribution and so on [106]. From the DoE results, it was found that the packing pressure has the biggest influence on the warpage. The packing phase is used to compensate for the shrinkage of the part during the cooling of the polymer melt; therefore, a high packing pressure leads to a better compensation of problems introduced by the shrinkage behaviour of the material. The increasing warpage with increasing melt temperature and the decrease in warpage with increasing mould temperature can be explained by the influence of the film insert. As described in chapter 2.2.3, the film insert can cause warpage due to its influence on the symmetry of the cooling process. According to Eq. 2-16, there will be two different heat flow rates in the areas where the film insert is. The heat flow rate towards the uncovered mould surface will be higher due to the higher thermal conductivity of the steel. The thermal resistance of the film insert will decrease the heat flow rate towards the mould surface covered by the film. This difference in the heat flow rates becomes more pronounced, the higher the temperature gradient between the mould and the melt is. A high mould temperature and a low melt temperature can, therefore, be expected to lead to the lowest amount of warpage caused by the film insert. Besides the contribution of the film insert, the larger contact area at the outside corners leads to differences in the cooling time between the in- and outside of the box shaped
part and the “spring-forward-effect”, which occurs due to differences in the in-plane and the thickness shrinkage will contribute significantly to the warpage [131].

A first attempt to verify the warpage found in the simulation on the moulded parts failed. A Zeiss UPMC 850 CARAT coordinate measurement machine was employed. Even at the lowest probing force of 0.5 N, it was found that the probe slipped at the surface and registered values in the direction perpendicular to the actual probing direction for some measurement points. Therefore, no reliable measurements could be obtained.

5.2.2 Iterations vacuum system design

The vacuum system which was designed to fixate the membrane on the core turned out to be the critical part of the mould design when the moulding experiments where started. The cross section of the initial design of the core insert with the according vacuum channel is shown in Figure 67. The vacuum pump was connected to the clamping plate of the mould on the movable plate. A channel inside this plate was connecting the pump to the 4 mm diameter channel in the centre of the core insert. From the narrower channel (diameter of 2 mm) of this centre channel at the top of the core insert, five channels with a diameter of 0.5 mm were used to distribute the vacuum to the sidewalls and the top of the core insert where the film insert was to be fixated.

The moulding experiments revealed that the film insert could not withstand the injection pressure and was penetrated by the melt. In a second iteration, the vacuum channel at the top of the core insert was sealed, since the melt hits the film insert in this section in a perpendicular direction with a
high velocity due to the increase in the flow rate at the small cross-section of the gate right on the opposite site of the cavity. Therefore, the impact on the film insert is quite high in this section.

Since the film insert was also penetrated at the sidewalls, microporous venting plugs (Strack Z139, diameter 1.6 mm) were used to avoid an unsupported area under the film insert, in a second iteration of the core design. With the available vacuum pumps, it was not possible to create a sufficient flow through these plugs to fixate the membrane.

Therefore, a third iteration of the vacuum system design was done. This time plugs with a diameter of 3 mm and a thickness of 1.2 mm were used. These plugs contained 31 laser-drilled micro-channels (see Figure 68). These channels offer a similar flow resistance to the first design, which is why the flow problem did not persist anymore. At the same time, the smaller diameter of the holes and the support sections in between reduced the mechanical stresses in the film insert, in comparison to the first design, when the injection pressure is acting on it.

![Figure 68: Plug with laser-drilled micro-channels](image)

**5.2.3 Container moulding**

For the injection moulding experiments for the container, an Engel ES 80/25 HL-Victory injection moulding machine was employed. This machine is a small conventional injection moulding machine with a screw diameter of 18 mm and a clamping force of 250 kN. The process settings can be found in Table 15.

The packing pressure was set to 70 % of the injection pressure. The packing time was defined by increasing the set time stepwise until no change in the part-weight was found. The injection speed corresponds to a flowrate of 10.2 cm³/s.
Table 15: Process parameter for injection moulding of the fuel cell container.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrel temperature in °C</td>
<td>235</td>
</tr>
<tr>
<td>Mould temperature in °C</td>
<td>50</td>
</tr>
<tr>
<td>Injection speed in mm/s</td>
<td>40</td>
</tr>
<tr>
<td>Packing pressure in bar</td>
<td>150</td>
</tr>
<tr>
<td>Packing time in s</td>
<td>2</td>
</tr>
<tr>
<td>Cooling time in s</td>
<td>10</td>
</tr>
</tbody>
</table>

When the SABEU membrane was used as the film insert in combination with the vacuum insert fixation system, the membrane was still penetrated by the mould and the vacuum channels were filled.

Therefore, the moulding experiments for the chosen material combination were conducted with the membranes fixated by double sided adhesive tape on the core insert. Even though this approach could produce useful parts, it was too unreliable. Only a fraction of the containers moulded showed an undestroyed membrane. In all the others, the adhesion of the double-sided tape between the core and the PET-membrane layer of the SABEU membrane was too good, and the membrane was destroyed during ejection (see Figure 70). At a lower injection speed of 20 mm/s, this problem was reduced, but the downside was that several short shots were produced with this setting.
As it can be seen in the topographical picture of the CO\textsubscript{2}-venting hole in Figure 71, this feature could be produced. This is clearly indicated by the structure of the non-woven membrane support at the bottom of the venting hole. The distortion at the wall of the hole indicates flash around the pin, which is protruding from the side wall of the cavity.

![Figure 70: Container moulded with SABEU-membrane and double sided tape: destroyed membrane (left-hand side), successfully moulded part (right-hand side)](image)

![Figure 71: Topographical picture of the CO\textsubscript{2} venting hole in a container with the SABEU-membrane](image)
Since the mechanical resistance against the injection pressure was found to be too low for the dual layer membrane, another membrane type was used. Even though the membranes by Porex were rejected in the material selection due to the large pore size and the resulting low pressure-resistance, they are advantageous when used as film inserts as they are made of a 250 µm thick PTFE-single layer. The disadvantage of these membranes, however, is that the safety margin for overpressure in the fuel container is drastically reduced, in case of venting problems.

Using the PM22ST-membrane by Porex, the containers could be moulded successfully (see Figure 72) when using the vacuum fixation system. Figure 73 shows the membrane attached to the core insert, fixed by the vacuum system before closing the mould. This membrane could withstand the injection pressure without being penetrated by the melt. Impressions of the venting channels could be found on the membrane after moulding (see Figure 74).

---

**Figure 72:** Successfully moulded container with Porex-membrane

**Figure 73:** Membrane fixated by vacuum system prior to moulding

**Figure 74:** Impressions on the film insert surface of a container moulded with the Porex PM22ST-membrane
Also, with this membrane the venting holes could be created successfully, even though flash that covered a section of the venting-hole could be found on one side (see Figure 75).

![Image of venting hole in container moulded with Porex-membrane]

**Figure 75: Venting hole in container moulded with Porex-membrane**

**Initial testing of the methanol retention properties**

For the validation of the container design, a sample of each container moulded with the SABEU-membrane and double-sided tape, and the Porex-membrane and the vacuum fixation system, were filled with neat methanol. The containers were closed with a lid, which was sealed with an O-ring as shown in Figure 76.

![Image of container filled with methanol and sealed by a lid]

**Figure 76: Container filled with methanol and sealed by a lid**

The methanol loss was investigated by the change in weight of the system over time. Therefore, the weight of the containers and the lids was measured with a Shimadzu AW220 electrical balance. The
standard deviation of this balance is ≤ 0.1 mg. Subsequently, the container was filled with neat methanol, and the weight was measured again. From then on, the weight was measured several times. The according plot based on a single experiment (see Figure 77) shows a significant decrease over time for both containers. The decrease in the linear fit of the system with the SABEU membrane was found to be 1.74 mg/hour.

![Figure 77: Change in Methanol stored in the container over time](image)

The slope for the system with the Porex-membrane is even steeper (4.55 mg/h). These values correspond to 2.2 µl/h and 5.75 µl/h which would be 26.4 % and 69% of the intended methanol volume and therefore way too high. During this experiment, no methanol leakage was visible. The methanol loss is, therefore, expected to be due to evaporation of methanol through the pores of the membrane. This would also explain the difference between the SABEU- and the Porex-membrane. The pore-size in the Porex-membrane is way bigger than in the SABEU, therefore the interface area between the methanol and the ambient air available for evaporation is way bigger. That could be the reason for a faster methanol loss. A first countermeasure to improve the methanol retention would be to reduce the size of the venting hole as far as possible concerning the CO$_2$-venting rate and the mechanical stability of the pin used for the creation of the venting hole in the mould. If this single sample experiment is confirmed, a re-design of the CO$_2$-venting system is inevitable.
5.3 Summary

In this chapter, the experimental investigations of the chosen material combination and the fuel cell container production were presented. These investigations were based on both the simulation of the film insert moulding process and the moulding experiments.

Testing the chosen material combination revealed blister formation due to a delamination of the PET-membrane layer. The blisters were found to form during the cooling phase of the injection moulding cycle. The blister height and the surface fraction of the blistered area were evaluated by a metrology routine developed for this purpose. A confocal laser scanning microscope was used to measure a 5 x 10 mm² area in the centre of the disc-shaped part in stitching mode. The blister height was evaluated based on Spk, and the ratio of the delaminated surface based on Smr1, using image metrology software. The obtained values were evaluated using a DoE-scheme and showed that blister formation mainly depends on the processing temperatures. The influence of the packing pressure was found to be less significant. A comparison with the simulation results showed similar trends in the average shrinkage under the film insert obtained by the simulation. In the simulation, however, no non-linear effects could be found, which differentiated it from the experimentally obtained effects. A possible explanation for this difference could be found in the use of a semi-crystalline material. The software used for the simulation does not offer the material properties required for the use of the implemented crystallinity model with the used material.

The simulations of the fuel cell container showed that the warpage in this part is mainly caused by the temperature difference between the melt and the mould. An increase in this difference increases the warpage. As for the material testing simulation, the influence of crystallinity on the warpage cannot be found by the simulation.

The vacuum system implemented in the core insert could not be applied with the chosen membrane. Using doubled sided tape instead of the vacuum system, and the use of another membrane type in combination with the vacuum system were used for the validation of the mould design.

An initial test of the methanol retaining properties of the container in a single sample experiment indicates insufficient methanol retaining properties.
6. Conclusion & Outlook

This work presented film insert moulding as a suitable process to produce plastic containers with the ability to vent CO\textsubscript{2} from the inside of the container, which can replace deep drawn metal containers for DMFC.

A detailed description of the material selection process has been given, which led to the choice of a dual layer membrane consisting of a nonwoven support made of polypropylene fibres and a porous PET membrane with an oleophobic coating to realize the venting function of the container. Polypropylene was chosen as overmoulding material due to its chemical resistance, its barrier properties for water and methanol permeation and its compatibility to the support material of the membrane.

Two mould designs have been presented, one for the initial testing of the compatibility of the chosen materials and a design based on a split mould for the container production.

The experiments conducted to test the material compatibility revealed that the use of the dual layer membrane can lead to blister creation in the surface of the membrane. This phenomenon has, to the author’s knowledge, not been described in literature before. Different tools were used to investigate the origin of the occurrence of blisters:

- Computed tomography scans
- Micro film insert moulding: In process monitoring with a high-speed video-camera
- Micro film insert moulding experiments following a full factorial Design of Experiments analysis
- Virtual overmoulding experiments by means of film insert moulding simulations.

The CT-scans revealed that the blisters are a result of delamination between the PET-membrane-layer and the non-woven support layer. This delamination process could be detected in the high-speed videos and took place during the cooling phase of the part.

Surface metrology was used to investigate the influence of the process parameters varied in the Design of Experiments analysis. For this investigation, a measurement routine was developed based on two surface roughness parameters, which are related to the height (\(Spk\)) and the surface fraction of the structures (\(Smr1\)) protruding from the core roughness. The routine was based on the measurement of a 5 x 10 mm\textsuperscript{2} area in the centre of the part employing the stitching mode of an Olympus LEXT 4100 confocal laser scanning microscope and was applied for the comparative measurement of the blisters. This metrological approach can be used for the definition of a suitable process window in FIM applications when e.g. new material combinations have to be tested.
The experiments showed a large influence of the processing temperatures $T_{\text{barrel}}$ and $T_{\text{mould}}$ and a weaker effect of the packing pressure on the investigated areal surface topography parameters, which were chosen as a comparable description of the blister covered area and the average blister height. Non-linear effects could be found for the main effects and the interactions of $T_{\text{barrel}}$. Apart from a weak interaction which might have an effect on $Spk$, a variation of the injection speed did not show significant changes in the blister behaviour.

Instead, the simulations showed a different order of importance of the influences. The investigated parameter, the average volumetric shrinkage under the film insert, mainly depends on $P_{\text{pack}}$, followed by weaker effects of the mould and the barrel temperature. Similar to the experimental results, the injection speed was not significant. The simulations only showed linear dependencies.

The discrepancy between the simulation and the experimental results can have several reasons. First of all, a direct comparison between the chosen parameters is not possible. Even if the volumetric shrinkage under the membrane is the main reason for the blister creation, a linear relationship between the shrinkage and the blister size and height is not necessarily a given.

On top of that, problems with the repeatability of the switch-over point between the speed controlled filling phase and the pressure controlled packing phase were discovered especially for runs with the high level of $T_{\text{mould}}$ in combination with the high level of $T_{\text{barrel}}$. This problem is suspected to be the main contributor to the non-linear behaviour found in the experimental results. Furthermore, this could contribute to an underestimation of the influence of the packing pressure in the experimental work.

A good agreement was found for the comparison of the filling patterns of the part between the high-speed videos and the simulations. Nevertheless, it is expected that the simplifications done in the simulations do affect the accuracy of the simulations, especially for the calculation of shrinkage. It is expected that changes in the morphology of the part and the related changes in shrinkage do affect the blister creation. This relation cannot be found with the used material models, since the crystallization effects are not taken into consideration. This problem could be overcome by an investigation of the crystallinity of the parts.

Eventually, it can be stated that blister free parts could be moulded with the chosen combination of materials. For a recommended process window, high mould temperature, medium barrel temperature and high packing pressure are expected to work best. A better control of the switch over point could lead to an improved part quality, when the high level of the barrel temperature is used.

Consequent experiments to produce the DMFC-container revealed that apart from the blister creation the chosen membrane causes further problems. Due to the insufficient mechanical stability of the 23 µm thin PET membrane layer, the vacuum fixation system in the mould could not be used with this membrane. Using double sided adhesive tape to fixate the membrane in the mould enabled injection moulding of the container but did not show satisfying results in the process repeatability. Replacing the membrane by a thicker, single layer PTFE membrane led to a successful production of the fuel cell container using the vacuum system for the fixation of the film insert.
An initial test of the methanol retention properties of the container revealed significant methanol loss. Therefore, a re-design of the CO$_2$-venting system is inevitable for a use of the container in DMFC applications.

Future work on this film insert moulded part has to focus on finding a reliable method for the validation of the geometric dimensions of the container, the validation of the methanol and water barrier properties, the re-design and validation of the venting function and investigations concerning the competitiveness of the FIM-part to the metal fuel cell container in the fuel cell application and if necessary further optimization of the part design, the material selection and the injection moulding process. The part design could be optimized based on the mould design presented in this work in terms of light weight design, the container shape or the maximization of the ratio between contained methanol volume and the total system volume. In this work, the focus regarding the part design was put on the production process. Furthermore, the area covered by the membrane and the position and the size of the venting holes must be reconsidered for an optimization of the performance of the fuel cell system.

For the final application of the presented process, namely the production of the containers, the use of further insert parts should be investigated. These parts are the valves necessary for refilling the fuel cell container as well as the anode cup. Using these additional insert-parts could be realized by implementing minor changes in the presented mould design. These metal parts can be used in an insert moulding process together with the membrane, and, thereby, further reduce the number of assembly steps for the entire fuel cell system. This step can save production time and costs regarding the mass production of the fuel cell system. The final step towards mass production would then be the automation of the process where pick and place robots can be used for automatic insertion of the insert parts.
References


Appendix

*DoE-settings for chapter 5.1*

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Acknowledgements

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