1 Introduction

1.1 Motivation and problem statement

The pultrusion process is a continuous and efficient manufacturing technology for Fiber Reinforced Plastics (FRP). Pultruded profiles out of these materials like Glass Fiber Reinforced Plastics (GFRP) or Carbon Fiber Reinforced Plastics (CFRP) feature unique properties regarding – among others – strength, stiffness and corrosion resistance at low density. While the pultrusion process has been established in industry for decades, new process developments can yet be very cost intensive. It is still common to solve process related problems by a trial-and-error approach based on the know-how of experienced operators [29]. Although this may be successful in many cases, such a series of trials can be very costly. This is especially the case for new adopters of the technology and inexperienced operators. Those issues inhibit the application of the pultrusion process for cost driven lightweight applications and hinder a more cost- and energy-efficient composite production. For those reasons, the development of an automated, closed-loop process control system is desirable, as it is not industrially available today. Despite individual approaches to achieving this goal, the fundamental basis for such a process control system in terms of a generic process understanding is still missing.

One prominent example for pultruded profiles are spar caps for wind turbine blades which represent an important and growing market for the pultrusion industry [115, 18]. Unidirectional reinforced CFRP or GFRP profiles are stacked within the FRP. The mechanical properties and the large amount of pultruded material required by this industry demands a manufacturing process that fulfills a reliant material quality as well as a high productivity. Therefore, the understanding of quality related process relationships and appropriate means for an efficient inline quality assurance gain in importance. At the same time, those two aspects build the necessary basis for a quality-oriented closed-loop control approach.

Plenty researchers have been working successfully on an improved process understanding based on mathematical models, however, due to the complexity of the process, those models are difficult to transfer to the industrial pultruders. Furthermore, not every effect and process situation can be modeled so far, leading to crucial gaps in a holistic process understanding.

Besides obvious challenges – like geometrical or dimensional complex profiles, the continuous handling of reinforcement textiles or a void-free fiber impregnation – also simple pultrusion profiles might still lead to severe processability issues. Especially epoxy resins, which offer along with polyurethane resins the best mechanical and thermal properties, are challenging to process in pultrusion due to their tendency to stick and cure inside the molding tool (die) [129]. Unstable process states, insufficient material quality and high scrap rates may be the result.

As a summary it can be stated that although the pultrusion process often is described as "automatable", it still cannot generally be controlled automatically from startup to steady-state, and experienced operators are not replaceable. Ongoing research is therefore necessary to reach a sufficient level of knowledge about the process itself as well as about appropriate process monitoring, quality assurance and process control methods to establish pultrusion as cost- and energy efficient technology for structural and high quality composite components in industries such as automotive or aerospace.

1.2 Objective and approach

The aim of this work is to contribute to closing the gaps in the automation of the pultrusion process by creating a basis for the development of an closed-loop process control system in terms of process knowledge and sensor technology. In order to achieve an appropriate advance of the current state of the art, the following *four objectives* are set:

1. Development of a theoretical basis for process analyzes of the pultrusion process by modified state-of-the-art process- and material models with temperature and process control algorithms.
2. Creating an experimental basis for efficient and data driven studies by implementation of a data acquisition system with in-situ (inline) process monitoring and quality assurance methods for pultrusion.
3. Identification and correlation of quality related, *steady-state* process variables as relevant input for a model based, closed-loop control approach.
4. Identification and correlation of quality- and control-relevant *transient* process variables or characteristics as input for a closed-loop control approach for startup and transient process situations.

For the fulfillment of these objectives, a multidisciplinary and data driven process analysis approach is developed and applied in a study that combines process simulation with appropriate process- and material-models, innovative sensor technology and experimental investigations with application of an inline data acquisition system.

2 State of the art in research and industry

The pultrusion process was developed in the 1950s and has gained in importance in the 1980s [122, 129]. The continuous process enables high production rates, which is why pultrusion can be described as one of the most cost- and energy efficient manufacturing methods for FRP. Although the basic process principle is simple, the variety of materials, geometries and process combinations as well as the versatile phyiscal and chemical process interactions make pultrusion a complex process. This Chapter gives an overview of the principles of the pultrusion process including process flow, processed materials and applications (Section 2.1), and summarizes the state of the art in context of this work. This includes process models for pultrusion (Section 2.2), quality criteria for pultruded profiles and means for process monitoring and quality assurance (Section 2.3) as well as process control (Section 2.4). While this Chapter focuses on a general overview of the relevant literature, important details of previous works are described and discussed in context of the respective Sections.

2.1 Principles of the pultrusion process

In the conventional pultrusion process (see Figure 2.1), reinforcement fibers in the form of rovings, non-wovens or fabrics are pulled through a thermoset resin bath or injection-unit and the fiber-resin-strand is cured in a heated die. The whole process is driven by reciprocating puller units or caterpillar pullers. The process is mainly controlled by the pull speed and the die temperature.

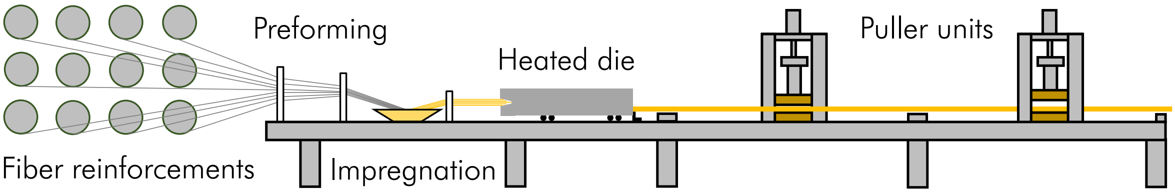


Figure 2.1: Pultrusion process with open-bath resin impregnation and reciprocating puller units

Several modifications and variations of the pultrusion process exist, in order to increase the geometrical degree of freedom, the choice of material to be processed or the material quality. The following special pultrusion processes are worth mentioning:

1. Resin Injection Pultrusion or Continuous Resin Transfer Molding [74, 59, 41]
2. Radius-pultrusion and the moving-mold concept for the production of continuously curved profiles [57, 58],
3. Pull-winding and pull-braiding, a combination of pultrusion and a winding or braiding preforming process [122, 16],
4. Pultrusion Resin Transfer Molding (PRTM) [52],
5. Prepreg based pultrusion processes like the Advanced Pultrusion Process (ADP) [20],
6. Pulshaping, a pultrusion process with a secondary shaping step [127],
7. Thermoplastic pultrusion processes like the reactive in-situ ε-caprolactam pultrusion [136, 153] or nonreactive processes based on commingled yarns or tapes [93, 155].

2.1.1 Processed materials

A pultruded profile is a composite material produced out of reinforcement fibers and a polymer matrix. Different types of fibers and reinforcement textiles can be processed in order to reach the desired material properties. In the international industrialized conventional pultrusion process, thermoset resins are used as matrix system mainly because of their low viscosity which is necessary for a good fiber impregnation in complex parts. The processing of thermoplastic polymers in pultrusion is still a niche but increased efforts have been done in the last couple of years in research and industry to accomplish first successful process developments and applications [60, 96, 107]. In order to tailor process and material properties, it is common to mix additives or fillers like into the liquid resin. An detailed overview about the most important fiber reinforcements, matrices and fillers is given below.

Fiber reinforcements [129, 115, 122]:
Glass fiber rovings and mats are the most commonly used reinforcements in pultrusion, mainly because of low costs and availability. A certain amount of 0° orientated fibers is always required to bear the pull forces during the process and the randomly orientated non-wovens assure a certain transverse strength. Carbon fibers exhibit a significantly higher stiffness but are significantly more expensive and not as widespread as glass fibers in pultrusion. Nevertheless, a fast growing market for carbon fiber based pultrusion are pultruded spar caps for wind turbine blades. For a increased strength and stiffness transverse to the

profile axis, fabrics and non-crimp fabrics can be processed. A special type of textile used in pultrusion are stitched complexes, a stacking of different textiles like rovings, fabrics, mats or veils. Surface veils or tissues are commonly used for an improved surface finish and as outer protection layer.

Matrices:
While the fiber reinforcement defines the main mechanical properties of composite materials in direction of their orientation, the polymer matrix significantly influences thermal properties, chemical resistance, interlaminar and impact strength and flammability [112]. The conventional pultrusion process is based on thermoset resins, especially *Unsaturated Polyester (UP), Vinylester (VE), Epoxy (EP), Polyurethane (PU), Acrylic* and *Phenolic* resins [122, 129]. Due to the different behavior in processing, thermoplastic polymers still represent only a negligible share of the industrially produced pultrusion profiles [93]. However, research focuses more and more on the processing of thermoplastic matrices in pultrusion and the interest in thermoplastic pultrusion is increasing also in industry. Thermoplastic composites do not only feature unique mechanical properties like an increased impact strength but also offer new opportunities for post-processing steps like welding or thermoforming. Furthermore, the meltable thermoplastic matrix enables more easily a second life for composite materials, even if a recycling process mostly decreases its mechanical properties due to shredded fibers.

UP and *VE* resins exhibit – beside their good mechanical properties – a good and adjustable processability and allow a high productivity because of their chemical reactivity [122, 129]. Compared to polyester resins, vinylesters offer superior impact and fatigue properties as well as a better chemical and thermal resistance. On the other hand, VE resins have a decreased reaction rate and are more expensive [112, 129]. In combination with their still rather low (UP) to moderate (VE) raw material costs, both resins lead to cost efficient products and therefore UP and VE resins are the most commonly processed resins in pultrusion [122]. One drawback of UP and VE resins is the need of styrene, which – dependent on the impregnation technology – may result in significant amounts of Volatile Organic Compounds (VOC) during production and the correlating health concerns. This is one reason why new operators of pultrusion partly avoid those styrene based resins.
Epoxy resins are more difficult to process due to their tendency to stick to the die-wall and their late point of gelation, but exhibit superior mechanical and thermal properties as well as corrosion resistance compared to UP and VE resins [129]. Besides those processing challenges, epoxy resins are more expensive than UP resins and result in slower line speeds, which in total makes epoxy based profiles pricier [129]. Latest developments in regard to processability and reactivity have

been making epoxy resins more attractive for pultrusion [38] and therefore they may play a more important role for pultrusion in the future.

Different tailored *PU* resins for pultrusion have been developed in the last decade [98, 82, 117], in order to provide a high reactivity along with increased elongation and toughness [129]. Two main sorts of PU resins exist for pultrusion, aromatic and aliphatic polyurethanes [123]. Aromatic polyurethanes are highly reactive resin systems for fast line-speeds and demand a metering and mixing equipment in conjunction with an injection chamber for impregnation [123]. While aliphatic polyurethanes might – dependent on the system – also be processible in an open bath, they offer an inherent ultraviolet-stability, good chemical resistance and anti-graffiti properties [123]. Compared to epoxy resins, PU resins might exhibit superior transversal and interlaminar shear strength [123].

Acrylic resins provide a particularly low viscosity, which makes them processible with high portions of fillers like the flame-retardant aluminum trihydrate [122, 129]. This feature in combination with a high reactivity and good mechanical properties enable applications for pultruded profiles where both, mechanical and Fire Smoke Toxicity (FST) requirements cannot be met with other resins [122, 76].

With respect to FST properties, *phenolic resins* exhibit the best behavior and feature a high fire resistance and produce low smoke under fire [122]. They also exhibit a high glass transition temperature and therefore good mechanical properties at elevated temperatures. However, since phenolic resins are condensation polymers, water is produced as by-product during reaction which makes – in addition to a high resin viscosity – the processing of phenolic resins in general difficult compared to other thermosets [122]. Furthermore, the compatibility of reinforcement and resin needs to be specifically assured for good mechanical properties and environmental emissions demand a high standard for workplace safety. [122, 129]

Thermoplastic pultrusion exhibits – except of reactive, in-situ polymerizing processes – a totally different chemical and physical behavior regarding processing and material properties. Both processes – the conventional pultrusion process and thermoplastic pultrusion – cannot be directly compared, and experimental results cannot be easily derived for the respective other polymer class. Therefore, thermoplastic matrices and processes and their respective literature are not further considered in this work, unless conclusions are independent of the matrix.

Additives and fillers:

Additives are mainly used for three purposes: to adjust the material properties, to improve the processability and to reduce costs. The most important process additive is the Internal Mold Release Agent (IMR) which reduces the tendency of the thermoset resins to adhere to the die-cavity surface (die-wall) [122]. IMR are typically fatty acids or waxes that are mixed into the resin and diffuse onto the polymer surface during polymerization [61]. The main task of the IMR is the build-up of a lubricating layer between the profile and the die-wall. Good release agents do not settle on the fibers and do neither reduce the mechanical properties of the profile nor affect secondary processes like painting negatively [122].

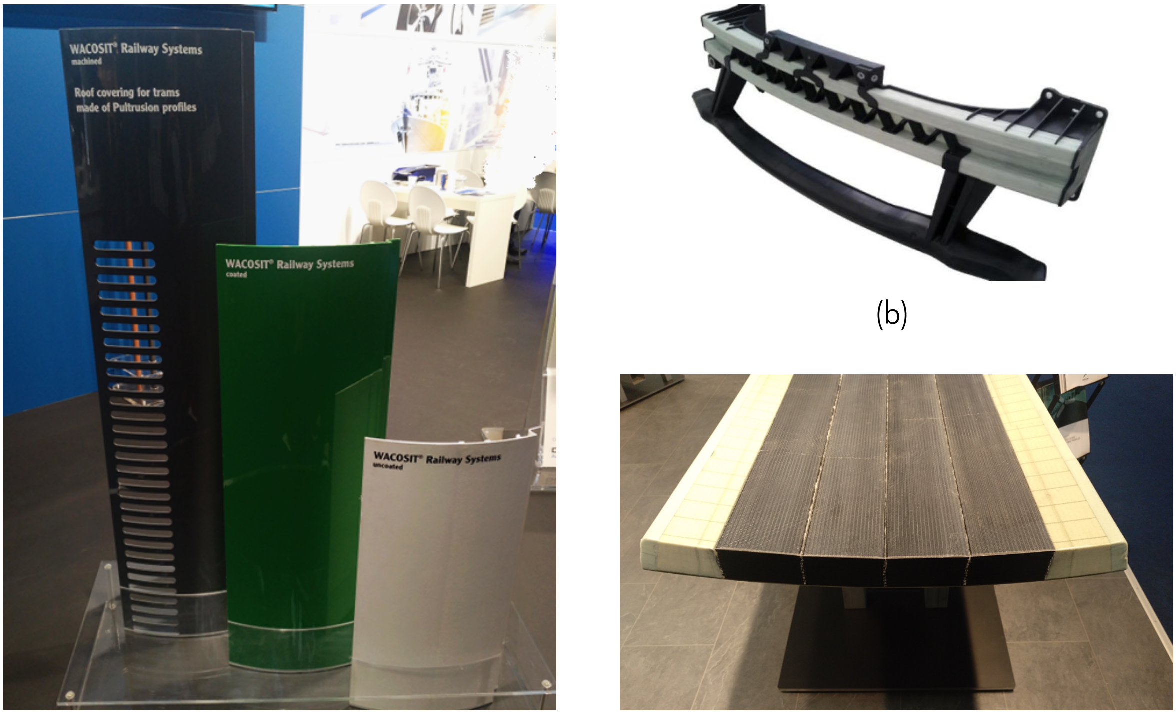
Commonly used powder fillers are calcium carbonate as cost reducing volume filler, clay for electrical properties and an improved surface finish and aluminum trihydrate for improved FST properties [129]. To reduce the surface effect of matrix shrinkage especially of UP and VE resins, so-called "low-profile" additives – mostly thermoplastic polymers – are dissolved in styrene and added to the resin [122].

2.1.2 Products and applications

The unique properties of pultruded profiles out of GFRP and CFRP enable various applications in different industries. These include especially construction, infrastructure, marine, transportation, energy as well as sports and leisure [129, 122, 144, 146]. Currently, pultrusion products exhibit a market share of about 5 % of thermoset based composites in Europe and an increased use of pultrusion is expected [154]. Besides applications in construction and infrastructure [154], the wind sector is expected to increase the demand for pultrusion profiles [115]. The below presented applications are divided into classical pultrusion products that are established for years or decades, and applications that began to gain importance within the last years or are expected to do so in the near future.

In general, composites offer major advantages over metals in corrosive environments. Therefore, pultruded GFRP profiles have been used for decades in structures like cooling towers, walkways, gratings and cable trays [129, 122], which demand a high durability under harsh conditions. Pedestrian bridges [122, 113] and lighting poles [33] are further examples for applications where durability but also an efficient installation due to lightweight are beneficial compared to conventional construction materials like steel and concrete. In transportation, interior and exterior panels for buses or trains are common pultruded GFRP products [122, 88] of which examples are shown in Figure 2.2a. Besides that, the good electrical insulation properties of GFRP have made pultruded profiles to an important material for – among others – high-voltage insulators [146] or nonconductive ladders [129].

One more recent application in the infrastructure and energy sector are pultruded hybrid CFRP/GFRP cables, that are used as lightweight core for electrical aluminum overhead conductors [51]. A growing and potentially large market for pultruded rods are rebars for building and bridge constructions as well as for repair applications [151, 21, 45]. Several innovative processes and products for pultruded rebars have been developed in the last years [99, 159, 155] and the good corrosion resistance can contribute to an increased durability of reinforced concrete constructions. In the automotive field two innovative pultrusion products are worth mentioning: a thermoplastic (Polyamid 6) GFRP front bumper crash beam [28] (see Figure 2.2b) and a radius pultruded CFRP rear bumper beam [87]. Enclosures for battery packs is another potential automotive application for pultruded profiles that is expected to bring major crash benefits for electric vehicles [44]. A longitudinal CFRP beam for lightweight chassis in commercial vehicles is one example of a pultruded profile in the vehicle's main structure [66]. One of the largest markets that is currently developing for pultruded CFRP profiles is however the wind energy sector. For the manufacturing of wind turbine blades, rectangular Unidirectional (UD) profiles are stacked and used as spar caps (see Figure 2.2c), bearing the main loads in the rotor blade [115, 18]. Due to the production and supply bottleneck of heavy-tow carbon fiber rovings, besides the stiffer CFRP profiles also GFRP is used for this application [114, 18].



(b)

(a)

(c)

Figure 2.2: Examples of pultruded profiles: (a) GFRP panels for railway applications, (b) thermoplastic GFRP front bumper beam [28], (c) stack of CFRP profiles for wind turbine blade

2.2 Pultrusion process models

Material modeling and process simulation is one efficient method to optimize the pultrusion process with regard to pull-speed and productivity, while taking into account certain quality criteria. A lot of research has been accomplished over the last decades on the development of pultrusion process models and corresponding material models, including the heat transfer in die and composite material, resin cure, fiber impregnation and resin pressure, internal stresses and distortion, and pulling force models [110, 6]. This chapter gives an overview of the relevant process models for this work, that partly have been applied and further modified in Chapter 5. The focus is set on heat transfer and cure models – applied for thermo-chemical simulations – as well as on process control models.

2.2.1 Heat transfer and cure models

Different mathematical approaches for modeling the heat transfer and cure in the pultrusion process have been developed for both steady-state and transient simulation. One of the first to develop a process model for pultrusion was Price [105] with a 1D heat transfer and pressure model with cure kinetics. Batch et al. developed a 2D heat transfer, cure, pressure and pulling force finite element model [15]. The first 3D heat transfer and cure model for pultrusion was published by Valliappan et al [143]. The model applies a control volume based finite difference approach for simulating an epoxy pultrusion process for a cylindrical rod in the die and post die and was validated by experimental temperature measurements. Several researchers later refer to this data to validate their simulation approaches [131, 83]. Lin et al. applied a more stable and efficient mixed time integration scheme as numerical approach in a general-purpose FE package for a transient and steady-state simulation for the same problem [83]. The latter approach is used as base for the process model developed in this work (see Section 5.2). A different numerical approach based on the Navier-Stokes-Equation and a porous thermal model has been applied by Barkanov et al. [11, 12]. Further work like the application of more efficient numerical approaches for transient and steady-state heat transfer and cure problems have been performed by Baran et al [8].

In order to improve the accuracy of the existing pultrusion process models, various process and material details were added in different investigations. Baran et al. added a variable thermal contact resistance at the interface between die-wall and profile and stated its influence on the temperature and cure as significant [9]. The effect of temperature- and degree-of-cure dependent material properties of the resin – the specific heat capacity, thermal conductivity, coefficient of thermal expansion (CTE) and density – on the pultrusion process were implemented by

Moschiar et al. [95] and also investigated by Joshi et al. [62]. The maximum calculated effect was a significant drop of the peak temperature (23 K) and thus a significant decreased degree of cure due to a total chemical resin shrinkage of 4 %, a CTE of $4.5 \cdot 10^{-6}$ 1/K and a linearly degree of cure dependent specific heat capacity and thermal conductivity (maximum +25 %) [62]. The influence on the peak temperature was dependent on the profile thickness. The relevance of temperature and degree-of-cure dependent material properties were highlighted as case-dependent.

Details about the above summarized mathematical models for heat transfer and resin cure are described in the Sections 5 and 4.2.1, respectively.

2.2.2 Holistic process models

Various works modify the above described thermo-chemical approaches by fluid-mechanical and pull force models to holistic, multiphyisical process models. Moschiar et al. combined a heat transfer and cure model with a pressure and pulling force model [95, 94]. Voorakaranam et al. developed a process model for injection pultrusion including resin flow, heat transfer and cure [147, 148]. The model was used to derive a linear regression model for the control of injection pressure, heating power and pull-speed, in order to assure a sufficient fiber impregnation and degree of cure at die exit. Furthermore, thermo-mechanical process models have been developed to simulate internal stresses and process induced shape distortion of pultruded profiles especially by Baran et al [10, 7].

2.2.3 Process control models

Beside process models considering a specific set of process parameters in steady-state condition, several works implemented transient process control algorithms. Voorakaranam et al. developed a process controller for resin pressure, temperature and pull-speed based on a steady-state, linear regression model derived from a 2D transient resin flow, heat transfer and cure simulation [147, 148]. Srinivasagupta et al. applied a 3D model for a similar process control objective and thus expands the scope of application to dynamic and non-linear problems, including a pull force analysis [121]. The same authors used the validated model to develop an algorithm for a multi-objective optimization of an injection pultrusion process. The objective function maximizes the production rate and further favorable considerations like controllability [120]. The latter is reached by reducing the thermal mass, which improves the dynamic response of the die to the heating power.

Barkanov et al. [13] implemented a temperature controller into a transient heat transfer and cure process model. The controller turns the power of electrical