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EVALUATING CLOSED RESIN-INJECTION-&-IMPREGNATION CHAMBERS FOR PULTRUSION PROCESSING OF AROMATIC PU-SYSTEMS AND METHYL METHACRYLATE RESIN SYSTEMS (ELIUM®)

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ABSTRACT

Pultrusion is a continuous process for production of fiber-reinforced polymer profiles with a consistent cross-sectional area. This study focuses on evaluating and optimizing the geometry of conical shape injection & impregnation chambers (ii-chambers) in the pultrusion process. Therefore, the following process parameters are investigated in this paper: four different opening angles of conical ii-chambers (ranging from 1.6° to 4.0°), various pulling-speed levels and aromatic-PU and PMMA resin systems, and also for two types of fibers: carbon-fibers (50 k) and glass-fibers (4800 tex). The influence of processing parameters in the pultrusion trials is assessed using three methods: 1) inspection of the profiles' surface quality, 2) quantitative analysis of pulling force with real-time data acquisition during the process, and 3) analysis of profiles' mechanical properties.

1 INTRODUCTION

1.1 Pultrusion process

In the pultrusion process, the profiles are shaped as defined by the cavity of the pultrusion-die, as the resin-impregnated fibers are consolidated, and the resin is polymerized ('cured') inside the cavity continuously.
Pultrusion is known for its high level of automation, high cost-efficiency in production and relatively low necessary investment of equipment, compared with other fiber-reinforced polymer processing techniques. Therefore, this highly efficient process is nowadays widely employed to produce a large variety of profiles for technical applications in many different areas – starting from 1 mm-diameter rods e.g., for medical applications, up to 1 m-high beams for roads, bridges, and infrastructures.
Amongst these many different profiles and application-areas the carbon-fiber reinforced bars for spar-caps inside wind-turbine blades and glass-fiber reinforced rods for reinforcement bars in concrete ('rebars') are two of the best known and most extensively used applications with pultrusion process.

1.2 Motivation of the study

While pultrusion offers many advantages and diverse applications, the quality of the final products and the manufacturing process itself can be influenced by various interdependent process parameters. Before entering the pultrusion die, the fibers must be impregnated with a suitable resin-system. The predominant method to achieve good impregnation is through an open-bath impregnation. However, certain resin-systems require the use of a closed device to achieve this impregnation. Aromatic Polyurethane (PU) is an example of such a system, which needs to be processed within a closed chamber due to its short pot-life of less than 20 minutes at room temperature [1]. Another example is PMMA (Elium) [2], which emits an unpleasant odor in its uncured state (monomer). Using a closed ii-chamber can help avoid or minimize the odor associated with PMMA during the impregnation process.

Besides the parameters opening angle of conical ii-chambers, different pulling-speed levels, and two different resin systems already mentioned above, it is worth noting that glass-fibers and carbon-fibers have significantly different permeabilities due to their different filament diameters. (glass ranging from 13 to 24 µm vs. carbon (typically) 7 µm)

1.3 Objective of the study

This article presents the results of a study that analyzes various combinations of process parameters and leads to an optimized set of parameters depending on the choice of resin systems and fibers.
Additionally, it offers valuable insights into potential future solutions for implementing closed-resin-injection-pultrusion in profiles with more complex cross-sectional areas, while exploring the utilization of new types of fibers and matrices.

2 METHODOLOGY OF THE STUDY

2.1 Setup of the pultrusion trials

2.1.1 Pultrusion machine

A pultrusion machine consists of several sections, starting with the fiber-creels and including upstream fiber-guides, resin-injection and impregnation devices, curing (inside the 'main'-pultrusion die), cooling, pulling system and cutting saw. The machine used in this study is equipped with a caterpillar puller which is capable to provide pulling force up to 10 tons for profiles up to 300 mm width, manufactured by Nanjing Loyalty and an automated process-data acquisition system.

Figure 1. Pultrusion machine, located at Fraunhofer Institute for Chemical Technology (ICT)

2.1.2 Pultrusion die and Injection impregnation chambers (ii-chambers)

Compared with conventional pultrusion process using open-bath impregnation, the injection and impregnation chambers (ii-chambers) attached to the entrance side of the 'main'-pultrusion die are necessary for the closed-injection-pultrusion. As shown in the following picture, all four ii-chambers were designed with the same principle, which have the same cross-sectional area of the entrance but different conical angles (ranging from 1.6° to 4.0°) and lengths (ranging from 450 mm to 800 mm).
The 'main'-die and all four ii-chambers were manufactured by the same mold maker, to ensure that any differences during the manufacturing process will be minimized.

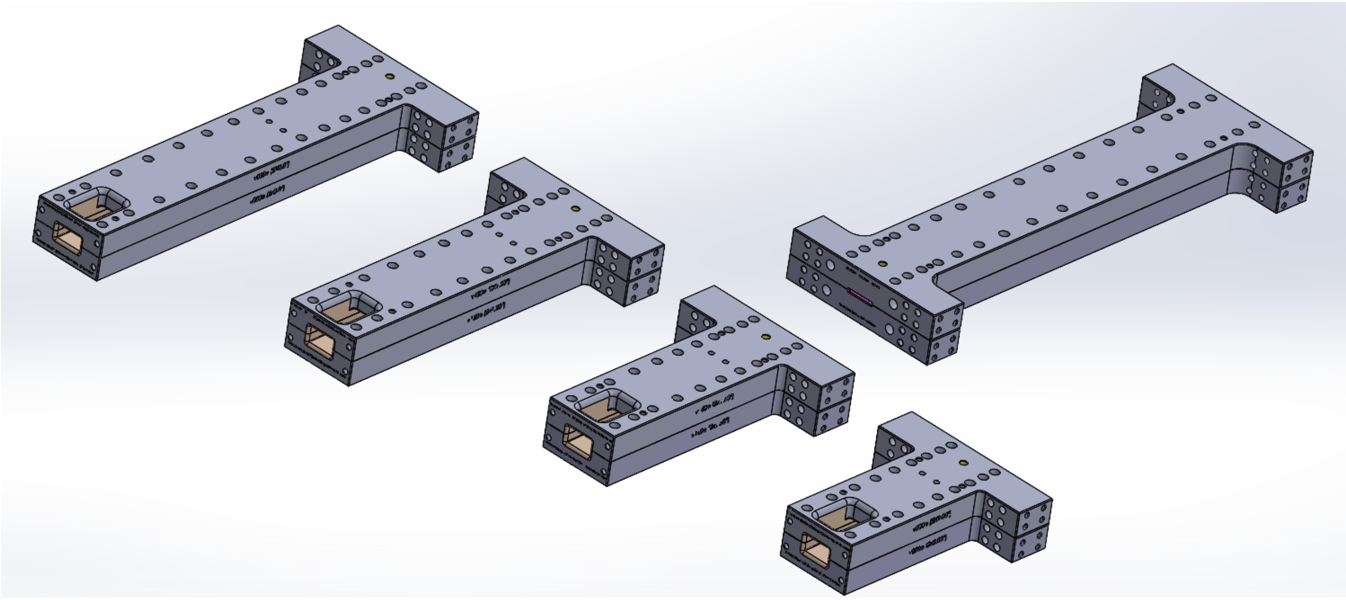


Figure 2. Pultrusion die to produce flat bars with 60 x 5mm cross-section and four bolt-on injection-impregnation chambers with different angles of conicity

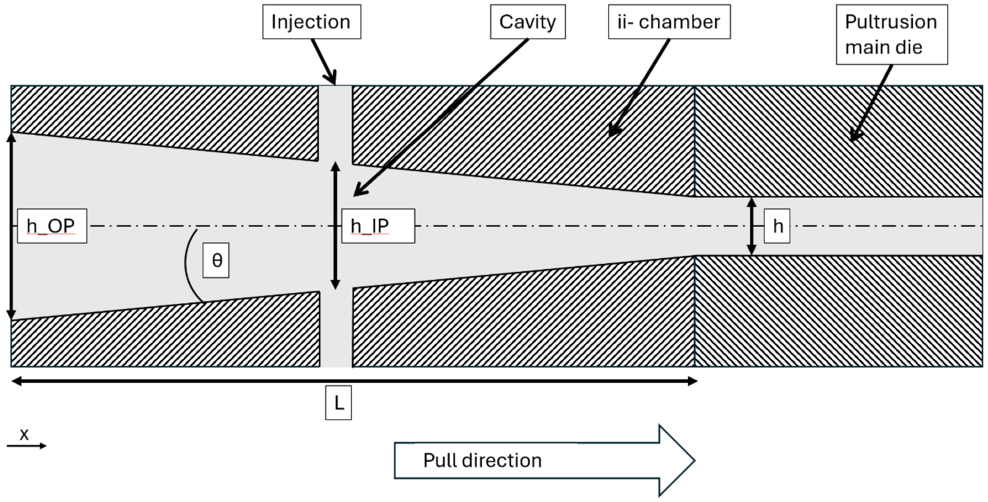


Figure 3. Sketch of opening angles in the ii-chambers

2.2 Raw materials used in this study

- Glass fibers:

Johns Manville StarRov 440-4800-090, 4800 tex, having multi-compatible sizing for Polyurethane, Epoxy, unsaturated Polyester and Vinylester and also compatible with PMMA (Elium). For this study, 106 rovings are used, with the final dimension of the profile this correspond to a fiber volume content of 65%.

- Carbon fibers:

Mitsubishi Pyrofil tow TRW40 50L, filament count of 50,000 and filament diameter of 7 µm. For this study, 96 rovings are used in the trials, with the final dimension of the profile this corresponds to a fiber volume content of 65%.

- Formulation of resin-systems:

Table 1 Formulation of resin

PU resin system	*Component 1*	*Component 2*	*Mold release*	*Peroxide*			*Viscosity*
1)	Isocyanate Desmodur 10PL**01**	Polyol Baydur 20PL20	IMR HB550				
parts by weight	133.65	96.15	3.85				200 mPa.s
2)	Isocyanate Desmodur 10PL**02**	Polyol Baydur 20PL20	IMR HB550				
parts by weight	130.77	96.15	3.85				40 mPa.s
PMMA resin system							
3)	Elium C595E		Zinc stearate	Perkadox 16	Laurox	Trigonox 141	
parts by weight	100		1	1	1	1	500 mPa.s

2.3 Design of experiment

The experiment setup described below (Table 1) was utilized to investigate the impact of different ii-chambers on the pultrusion process and properties of pultruded profiles. Four main parameters – opening angles of ii-chambers, levels of pulling speed, matrix, fibers varied during the pultrusion trials. The table provides a comprehensive overview of the experiments and parameter combinations, resulting in a total test field of 48 parameter configurations.

The main comparing parameter are the four different opening angles of the ii-chambers, so that all the four ii-chambers have been applied to the trials with three different resin systems (PU_10PL01, PU_10PL02, PMMA_Elium_C595E).
The trials with PU resin and glass fiber were carried out at pull speed levels of 0.5, 0.7, and 0.9 m/min.
The trials with PU resin and carbon fiber are planned to be carried out in the next a couple of months, due to the capacity of the machine and personnel.

For the trials with PMMA resin, glass-fiber and carbon-fiber were utilized at pull speed of 0.3, 0.4, and 0.5m/min. Due to the different curing kinematic of resin systems, trials with PMMA resin systems were not carried out at the pull speed levels higher than 0.5 m/min. Once the pull speed higher than that, not fully impregnated and cured fiber bundles were observed, which made it difficult for further analysis with surface quality and mechanical property tests.

Table 2. Parameters in the trials

Fiber-Type	ii-chamber (2 x θ°)	Pull speed, v [m/min]					
		0.3	0.4	0.5	0.5	0.7	0.9
		PMMA Elium			Polyurethane		
Glassfiber	2 x 2.0°	GF_C595E			GF_10PL01		
					GF_10PL02		
	2 x 1.6°	GF_C595E			GF_10PL01		
					GF_10PL02		
	2 x 1.2°	GF_C595E			GF_10PL01		
					GF_10PL02		
	2 x 0.8°	GF_C595E			GF_10PL01		
					GF_10PL02		
Carbonfiber	2 x 2.0°	GF_C595E					
	2 x 1.6°	GF_C595E					
	2 x 1.2°	GF_C595E					
	2 x 0.8°	GF_C595E					

3 RESULTS AND ANALYSIS

3.1 Pulling force analysis

Pulling force is a measured value determined by several boundary conditions (e.g., shape of the profile, fiber volume content) and parameters (e.g., pulling speed) of the pultrusion process. On-line monitoring of pulling force can also be an evaluation of the profile quality and the pultrusion process itself. The integrated pulling force sensor attached to the pultrusion machine has a measuring range up to 100 kN and a sampling rate of 1 Hz.

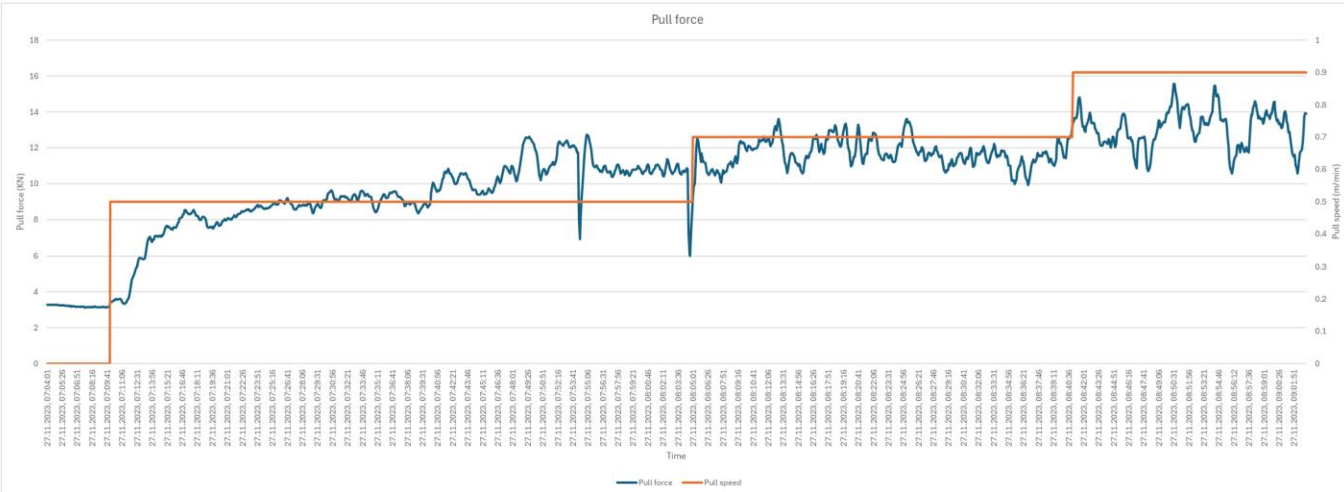
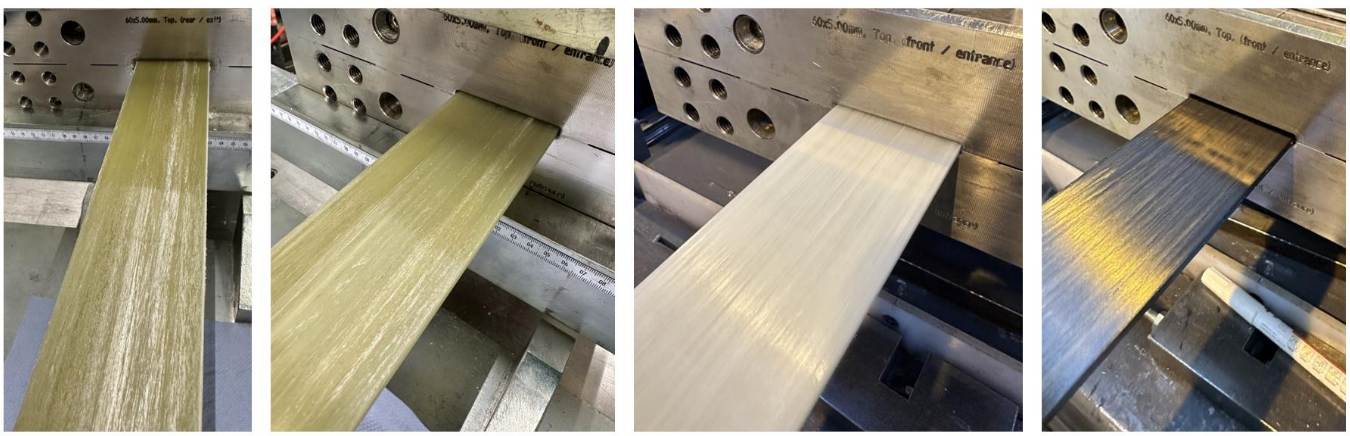


Figure 4. Pulling force’s time series graph of a trial with 0.5, 0.7 and 0.9 m/min, glass fiber, 10PL01, 2x2.0°.



1) 2) 3) 4)

Figure 5. 1) Profile based on PU_10PL01, glass fiber 2) Profile based on PU_10PL02, glass fiber 3) Profile based on E595C, glass fiber 4) Profile based on E595C, carbon fiber.

3.1.1 Pulling speed levels

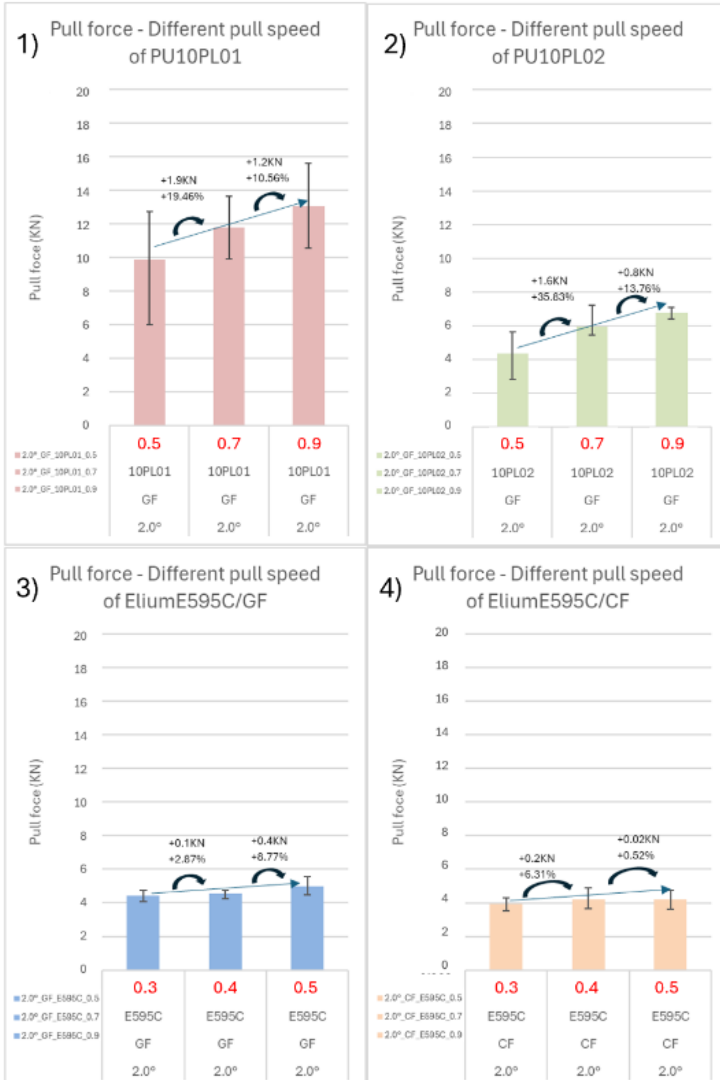


Figure 6. Pulling force vs. different speed levels – all with 2 x 2,0° ii-chamber: 1) glass fiber, PU_10PL01. 2) glass fiber, PU_10PL02. 3) glass fiber, E595C. 4) carbon fiber, E595C.

The figure 6 shows 4 examples of the average pulling force measured during the pultrusion with the same ii-chamber (2 x 2.0°) and different speeds of each combination of fiber and resin system. The result shows a clear trend throughout all combinations of fiber and resin systems, that pulling force increases with higher pulling speed.

3.1.2 ii-Chambers with different opening angles

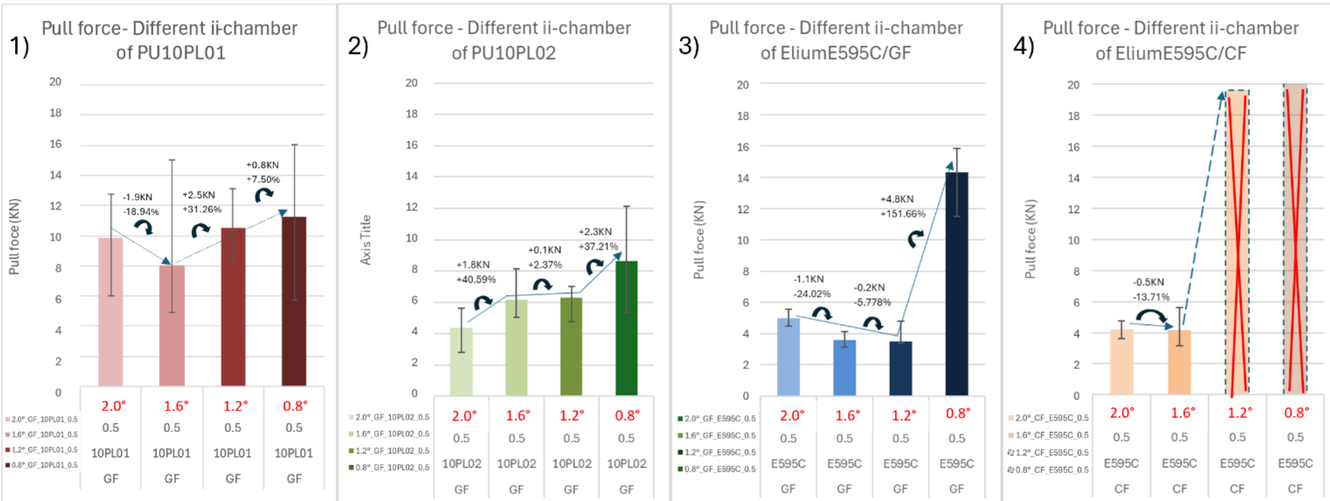


Figure 7. Pulling force vs. different ii-chambers, all with 0.5 m/min. 1) glass fiber, 10PU01. 2) with 0.5 m/min, glass fiber, 10PU02. 3) with 0.5 m/min, glass fiber, E595C. 4) with 0.5 m/min, carbon fiber, E595C.

The figure 7 compares the pulling force measured during the pultrusion process ii-chamber with different opening angles but the same pulling speed (0.5 m/min) for all combinations of fiber and resin systems. Each combination of fiber and resin systems shows a different trend when changing ii-chambers. However, all combinations of fiber and resin systems with 2 x 0.8° show the same result, having the highest pull force among all results measured.

- For glass fiber and PU_10PL01, the lowest pulling force appears at 2 x 1.6° opening angle. The pulling force reduces from 2 x 2.0° to 2 x 1.6°. After the lowest point at 2 x 1.6°, the pull force increases again when using ii-chambers with smaller angles.
- For glass fiber and PU_10PL02, the lowest pulling force appears at 2 x 2.0°. It increases with a smaller opening angle. From 2 x 1.6° to 2 x 1.2°, the pull force only increases a small amount.
- For glass fiber and PMMA (Elium), the lowest pull force shows at 2 x 1.2°. The pull force decreases with a smaller ii-chamber angle. From 2 x 1.2°to 2 x 0.8°, the pulling force increases significantly.
- For carbon fiber and PMMA (Elium), from 2 x 2.0° to 2 x 1.6°, the trend of pulling force decreases with the decrease of opening angle. For 2 x 1.2° and 2 x 0.8°, extremely high pulling force was observed during the pultrusion process, which is out of the range of measurement and also reached the upper limit of the puller, so that the process was stopped.

3.1.3 Different resin systems

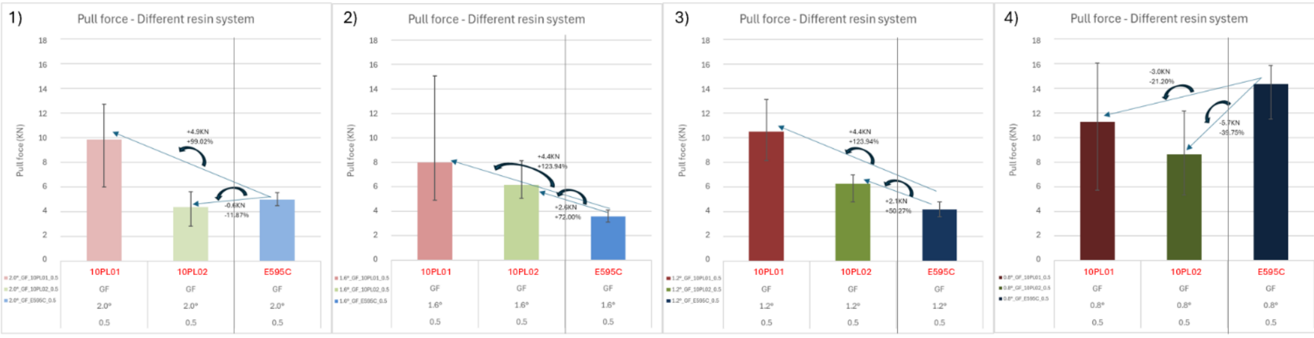


Figure 8. Pulling force of different resin systems, all produced with 0.5 m/min, 1) glass fiber, 2 x 2.0°. 2) glass fiber, 2 x 1.6°. 3) glass fiber, 2 x 1.2° 4) glass fiber, 2 x 0.8°.

The figure 8 compares the pull force measured during the pultrusion process of different resin systems, with the same ii-chamber opening angles and pulling speed. The average pulling force of glass fiber with PU_10PU02 is observed to be lower than that of glass fiber with PU_10PU01, attributed to the lower viscosity of the isocyanate 10PL02. This trend persists across various pulling speeds. Additionally, when comparing Elium to PU_10PL01 with ii-chamber angles of 2 x 2.0°, 2 x 1.6°, and 2 x 1.2°, Elium exhibits lower pull force. However, at an ii-chamber angle of 2 x 0.8°, the pull force of Elium notably increases, surpassing that of PU_10PL01.

3.2 Surface roughness measurement

As one of the important evaluation criteria, the surface quality of the pultrusion profiles is measured by the Mahr MarSurf M 300 + RD 18 instrument, employing a tactile surface measurement method with a stylus. According to DIN EN ISO 4287 standard [3], measuring both the arithmetic average roughness (Ra) and the average peak-to-valley height (Rz), with a measurement range of 350µm over a traversing length of 17.5mm. The fibers are pull through the pultrusion die only in the longitudinal direction, so the surface roughness in the transverse direction which is expected to be rougher than longitudinal direction roughness was measured and used for the surface analysis of the profiles [4].

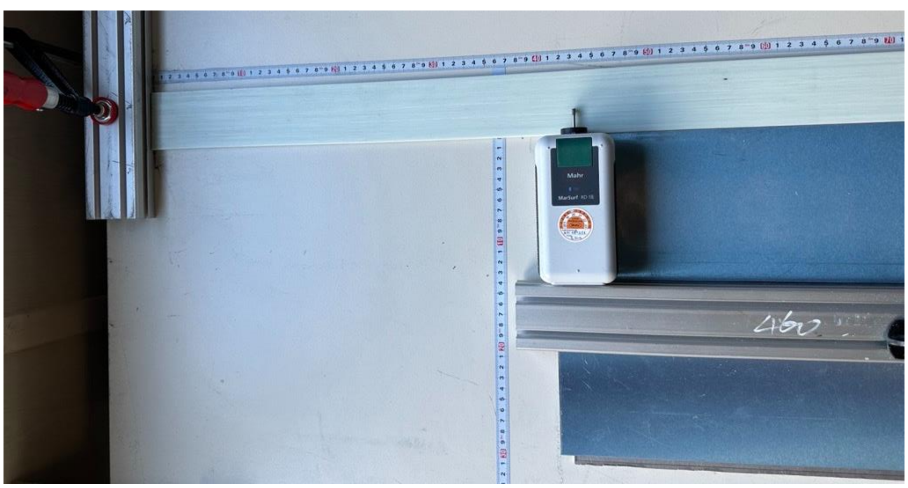


Figure 9. Setup of the surface roughness measurement device (top view). Measurement taken perpendicular to pulling direction.

3.2.1 Pulling speed levels

Analog to the results of pulling force, as the pulling speed increases, the surface roughness of the profiles also increases. The findings reveal a consistent trend across all combinations of fiber and resin systems.

3.2.2 ii-Chambers with different opening angles

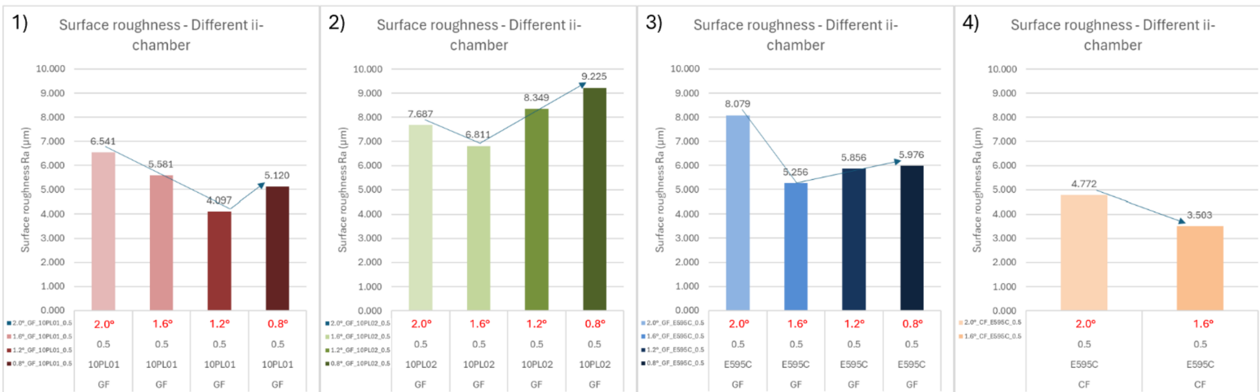


Figure 10. Surface roughness of pultruded profiles produced using different ii-chamber – all with 0.5mm/s 1) glass fiber, 10PU01. 2) glass fiber, 10PU02. 3) glass fiber, E595C. 4) carbon fiber, E595C.

The figure 10 shows the highest surface roughness (Ra) measured with the same pulling speed but with different combinations of fiber and resin systems. All combinations of fiber and resin systems show a different trend when changing ii-chamber angles. The surface roughness of different ii-chamber configurations displays unique trends depending on the combinations of fiber and resin utilized. Nonetheless, comparing this trend with the pulling force with different ii-chambers, a deviation in the trend becomes more obvious.

3.2.3 Different fibers (glass fibers vs. carbon fibers)

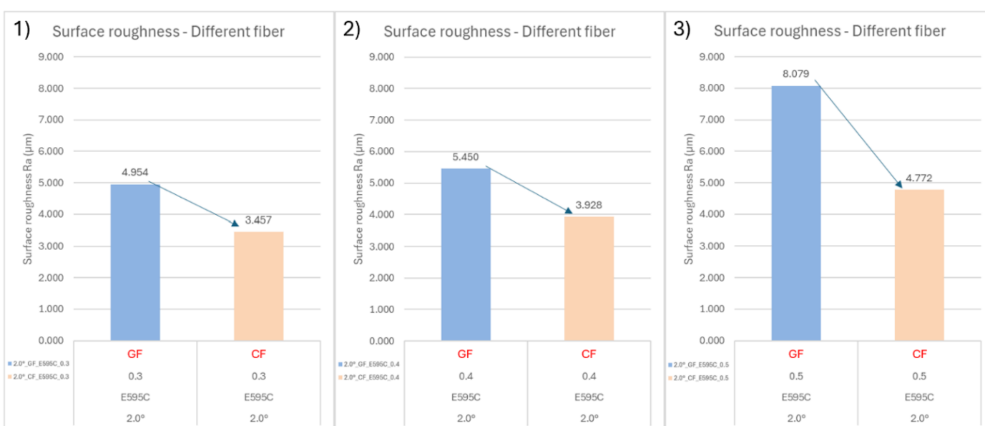


Figure 11. Surface roughness of pultruded profiles based on Elium. Comparing different fibers and pulling speeds.
1) 0.3 m/min, 2 x 2.0°, E595C 2) 0.4 m/min, 2 x 2.0°, E595C 3) 0.5 m/min, 2 x 2.0°, E595C.

The figure 11 shows the highest surface roughness (Ra) measured under the same pulling speed and ii-chamber opening angles. Comparing different fibers with PMMA (Elium) resin system, carbon fiber exhibits lower surface roughness in comparison to glass fiber, attributed to its smaller filament diameter when compared to glass fiber.

3.3 Mechanical property tests

Three-point bending test is selected to evaluate the mechanical properties of the pultruded profiles. The test follows the standardized procedure outlined in DIN EN ISO 14125 [5]. The dimensions ratio of the samples is determined by the standard, as it accounts for the constraints posed by the geometry of the pultrusion die. Likewise, the machine setup, including span distance and testing speed, adheres to the definitions outlined in the standard.

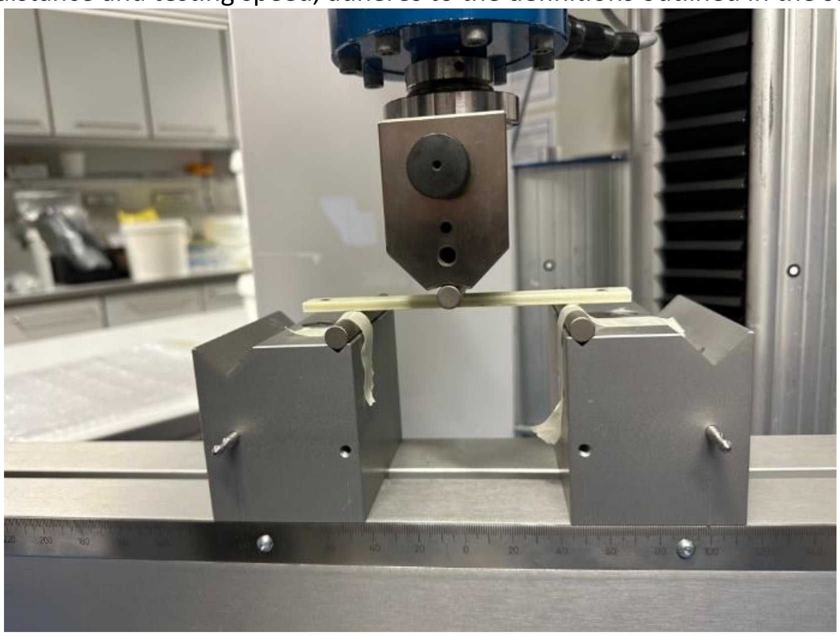


Figure 12. Setup of the Three-point bending test.

3.3.1 E-modulus

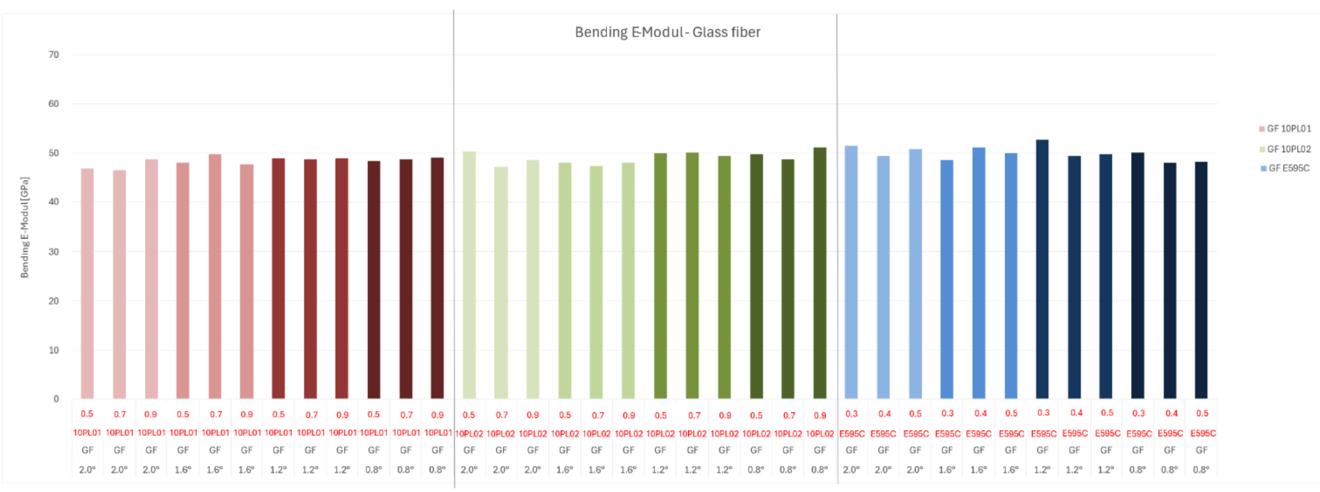


Figure 13. E-modulus (3P-bending) of all glass fiber reinforced profiles

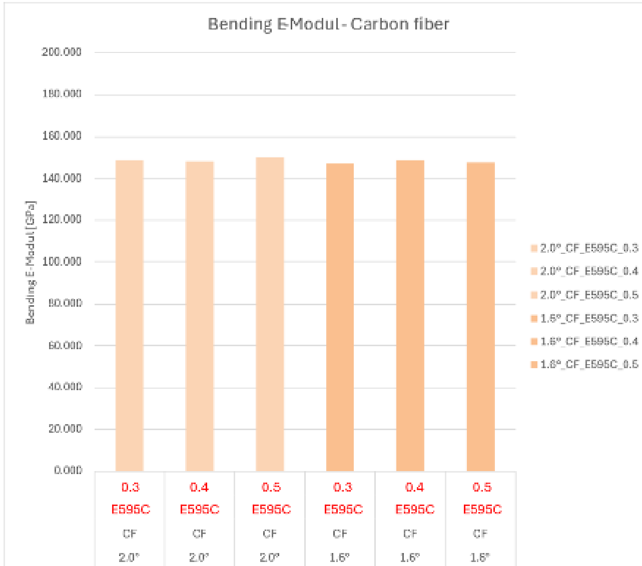


Figure 14. E-modulus (3P-bending) of all carbon fiber reinforced profiles

The bending E-modulus results for both glass fibers and carbon fibers reinforced profiles consistently fall within a very similar range. This consistency underscores the dominant influence of fiber type on the bending E-modulus, as evidenced by the closely aligned ranges observed across the different fibers.

3.3.2 ii-Chambers with different opening angles

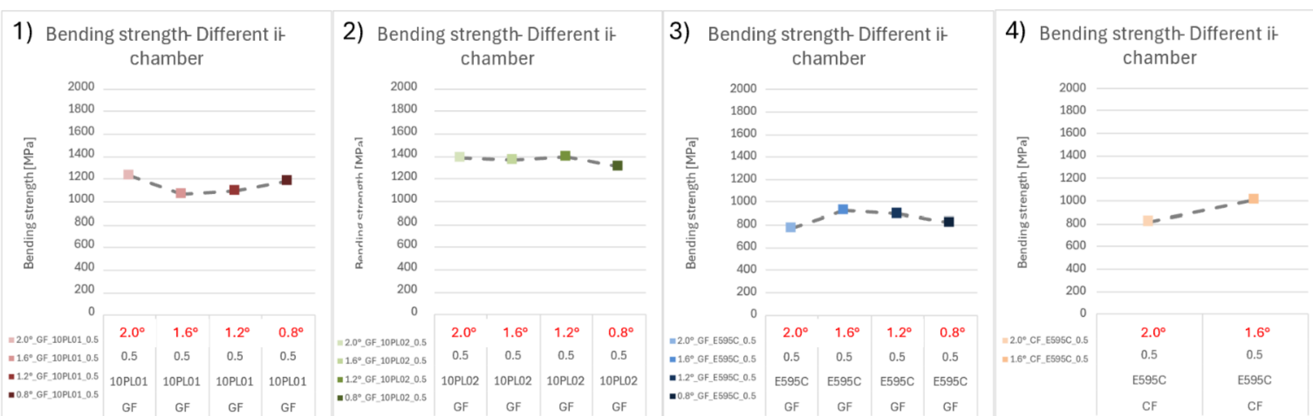


Figure 15. Bending strength of profiles produced using different ii-chambers, all with 0.5 m/min
1) glass fiber, PU_10PL01 2) glass fiber, PU_10PL02 3) glass fiber, E595C 4) carbon fiber, E595C.

The figure 15 shows the bending strength of the different ii-chamber angles with same pull speed (0.5m/min), same fiber and same resin system. When comparing the ii-chamber angles, the bending strength does not exhibit a distinct trend, as the deviations among bending strengths are minimal.

4 SUMMARY AND OUTLOOK

Based on the analysis of the pulling force during the process, surface quality and mechanical properties of the pultruded profiles, the trends observed can be summarized as follows:

- When comparing different pull speed levels, both pull force and surface roughness demonstrate a consistent trend: as the speed increases, the measured parameters will also increase.
- When examining the opening angles of ii-chambers (2 x 0.8° to 2 x 2.0°), differing trends are observed between pulling force and surface roughness. Lower pulling force during the process doesn't always exhibit a better surface quality.
- The resin system PU_10PL01 has higher average pulling force, while the surface quality of the profiles is better than those with PU_10PL02 and PMMA(Elium) resin systems.
- When comparing various resin systems, distinct characteristics emerge:
    - Trials with PU_10PL01 showed higher pulling force, resulting in better surface quality and with moderate bending strength of the profiles.
    - Conversely, trials with PU_10PL02 demands lower pull force, yielding worse surface quality, yet high bending strength of the profiles.
    - Meanwhile, trials with PMMA (Elium) E595C displayed relatively low pull force, generating moderate surface roughness, albeit with lower bending strength of the profiles.
- When comparing trials with different fibers, the pulling force shows no significant difference between glass and carbon fiber within the PMMA (Elium) resin system at the angles of 2 x 2.0° and 2 x 1.6° of glass fibers. However, the surface roughness of the profiles is notably better when employing carbon fiber.

The Hardware and Design of Experiment (DoE) used in this study will be applied to further pultrusion trials with other process parameters (e.g. other resin systems) to investigate related research topics.

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