



M Ű E G Y E T E M 1 7 8 2

BUDAPEST UNIVERSITY OF TECHNOLOGY AND ECONOMICS

FACULTY OF MECHANICAL ENGINEERING

DEPARTMENT OF POLYMER ENGINEERING

GÉZA PATTANTYÚS-ÁBRAHÁM DOCTORAL SCHOOL OF MECHANICAL ENGINEERING

# DEVELOPMENT OF T-RTM TECHNOLOGY AND A COATING METHOD

PHD THESIS BOOKLET

Author: **Orsolya Viktória Semperger**  
mechanical engineer

Supervisor: **András Suplicz, PhD**  
assistant professor

BUDAPEST, 2022

The reviews of the doctoral dissertation and the written report of the defence procedure are available at the Dean's Office of the Faculty of Mechanical Engineering of the Budapest University of Technology and Economics.

## 1. INTRODUCTION

Nowadays, the automotive, water and air transport and the sporting goods industries and the military are developing very rapidly. In these sectors the most important goal is to develop materials and their composites which have low density (and therefore reduced weight) and good mechanical properties (such as high strength or stiffness), so that they can be used as load-bearing parts. Reducing production cycle time should be a major factor throughout the designing process. Low consumed energy use during production and the recyclability of the product are also important aspects. In recent decades, numerous materials and technologies have been developed to this end.

Composite materials play an important role among technical parts. One of the great advantages of polymer composites is that their density is far lower than that of steel and aluminium, thus a significant weight reduction can be achieved with their use. The reduction in weight necessary to comply with the regulations of carbon dioxide (CO<sub>2</sub>) emissions of cars, with internal combustion engines. The maximum permissible value is 95 g/km by 2020 and 75 g/km by 2030 for new cars. The automotive industry accounts for a very large proportion of the use of composites.

Today, in addition to the complexity of the product, recyclability is a basic requirement, which can be done with thermoplastic polymer matrix composites. Thermoplastic polymers have good stiffness and heat resistance, and high strength, but their spread is inhibited by the fact that some fiber reinforcement materials can only be properly impregnated with difficult or complicated processes. The reason for this is that the viscosity of polymers in the molten state is very high (10–100 Pa·s). In the automotive industry, mass production can only be maintained with a high level of automation. A good solution to this problem can be the use of  $\epsilon$ -caprolactam (CL), which has low viscosity (3–5 mPa·s) in the molten state and, through anionic ring-opening polymerization forms polyamide 6 (PA 6). Caprolactam has been known as a raw material for a long time, primarily in the field of polyamide fiber production. The research so far has mainly focused on optimizing and speeding up the polymerization process, and expanding the product range. Recently, in the field of composites, there has been an increase in the number of studies focusing on the impregnation of various reinforcing textile systems (glass fiber (GF), carbon fiber (CF), woven, non-woven and hybrid systems). Regarding what additives can be added to the polymer matrix and how its properties can be modified, there is currently little literature available, although it has become an increasingly popular research topic in the last 5 years.

Thermoplastic resin transfer molding technology (T-RTM), was developed on the basis of resin transfer molding (RTM), which originally processed thermosetting plastics, and is a highly productive and highly automated process that can also be used in industrial conditions. The experience gained during the development and production of anionically polymerizable CL (which is called castable or reactive

polyamide and is used in semi-finished products, films, and pipes) provided a good basis for its special processing. The novelty of the developed T-RTM process is that the system can be easily automated and CL is mixed with the activator and the initiator in a way that the reaction starts only in the mold (in situ) after injection, and polymerization is completed in few minutes. The procedure takes place in a closed system in an environment perfectly free of moisture. The special feature of the polymerization process is that it takes place below the melting point of PA 6, so liquid CL is transformed into solid polyamide without the polymer ever melting. During polymerization, a thermoplastic polymer is obtained that does not contain crosslinks. In the case of composite production, the preformed reinforcing material, potentially in a special layer order, is placed in the lockable, tempered mold. If the properties of the composite need to be modified, certain grainy additives cannot be used during the traditional process, because they are filtered out by the fabric, thus creating inhomogeneity in the product. Therefore, a functional coating layer is needed on top of the composite layer, which contains the necessary fillers and additives.

The main goal of my research is to develop of a T-RTM process that is suitable for both the creation of fiber-reinforced composites with a PA 6 matrix from the anionic ring-opening polymerization of CL, and the production of a surface coating based on the same PA 6 material, but modified with additives for a specific application. In order to develop this complex system, I needed to examine the properties of PA 6 produced by anionic ring-opening polymerization, and also the additives and fillers, and their effect on the polymerization process and the properties of PA 6.

## 2. CRITICAL ANALYSIS OF THE LITERATURE, OBJECTIVES

In my research, I divided the researched literature into four main groups. The first area was studies on PA 6 produced from CL. I also studied the effect of the production technology parameters on the properties of the PA 6. However, I found that the researches were conducted on small samples and under laboratory conditions. From the point of view of industrial applicability, production cycle time is an important feature, therefore its reduction is desirable. The process suitable for automated production is the T-RTM technology, which is still an under-researched field due to its novelty.

There is little literature available on the moisture absorption of PA 6 produced from CL, even though it is an important field, as moisture greatly affects the mechanical properties of PA 6. The investigation of the effect of different relative humidities and an aqueous media on the water absorption process of PA 6 is also a little researched area.

I studied the appropriate distribution of additives and their effect in order to change the properties of CL. Very few studies are available on TiO<sub>2</sub> with CL, which is often used in case of polymers. Sedimentation occurs during the dispersion of additives in CL, due to the low viscosity of the matrix, which has not yet been investigated.

The homogeneous distribution of the additives is also hindered by the reinforcement in the composite layer, so in order to eliminate this, it is necessary to create a coating layer. One of the most environmentally friendly and efficient ways to do this is the use of IMC technology. This method has not yet been used by any research group in combination with T-RTM, during which the base and the coating layer were both PA 6.

Finally, I studied the physical recyclability of PA 6. In the large amount of literature that I examined, no one investigated the physical reprocessing by injection moulding of PA 6 produced from CL by T-RTM technology.

Based on the literature review, I set the following aims:

1. I will study the effect of the production parameters of T-RTM on the thermal, mechanical and morphological properties of PA 6.
2. I will develop a doping method of the CL system and examine the sedimentation of additives, depending on their type, size and surface treatment.
3. I will investigate the effect of additives on the UV resistance of PA 6 produced by anionic ring-opening polymerization.
4. I will investigate and model the moisture absorption capacity of doped and non-doped PA 6 samples with different crystalline fractions at different relative humidities.
5. I will develop a coating process for PA 6 produced from CL by T-RTM, by anionic ring-opening in situ polymerization.
6. I will examine the adhesion between the preform and the coating layer, and analyse the deformation resulting from the different shrinkage of the two layers.
7. I will examine the recyclability of PA 6.

### 3. MATERIALS AND METHODS

#### 3.1. Materials

##### $\epsilon$ -caprolactam – initiator – activator system

For the production of the test samples, I used a system consisting of  $\epsilon$ -caprolactam, initiator and activator, which can be used for the production of cast PA 6 produced by in situ anionic ring-opening polymerization with a short cycle time, at temperatures between 130 and 170 °C, which is below the melting point. The monomer is  $\epsilon$ -caprolactam - CL (AP-Nylon, L. Brüggemann GmbH & Co. KG, Germany), which has a melting point of 69 °C, a boiling point of 270 °C and a viscosity of 3–5 mPa·s in the liquid state. The initiator is sodium caprolactam (Brüggolen C10, L. Brüggemann GmbH & Co. KG, Germany), which has a melting point of 62.2 °C. Like CL, it is sensitive to moisture and is easily deactivated in the presence of water. The activator is hexamethylene-1,6-dicarbamoyl caprolactam (Brüggolen C20P, L. Brüggemann GmbH & Co. KG, Germany). Its melting point is 70 °C. Due to the hygroscopic nature and light sensitivity of the raw materials, I stored them in an aluminum bag at 40 °C under a vacuum of 500 mbar after opening. The maximum allowed moisture content of the raw materials is 0.01%. During the production of the test specimens, I worked with the following raw material proportions: CL – 92.5 m/m%, C10 – 4.5 m/m%, C20P – 3 m/m%. Contrary to the manufacturer's recommendation, I increased the amount of initiator (2.2 m/m%) and activator (1.5 m/m%) used, to accelerate the polymerization process. This was important for industrial usability (shorter cycle time), and for the compensation for possible moisture content.

##### Additives

The additives used during the tests and their main properties are shown in Table 1. To achieve the required properties from the large selection of additives, I selected the ones used based on the data published by the manufacturers. Before using the additives, I dried them for 8 hours in a drying cabinet at a temperature of 80 °C.

Name	Manufacturer, product name	Particle diameter	Type	Surface treatment	Jelölés
Graphite	Imerys, Timrex C-Therm	150 $\mu$ m	-	-	G
Talcum	IMIFABI, HTPultra5L	650 nm	-	-	TA
Grinded graphite fibre	Zoltek, Panex Milled Fiber, PX35-MF200	150 $\mu$ m	-	-	MCF
Titanium dioxide	KOLTEX, KTR600	45 $\mu$ m	rutile	aluminium, silicon	TiO <sub>2</sub> $\mu$
Titanium dioxide	SkySpring Nanomaterials Inc., P.N.: 7920DL	10-30 nm	rutile	-	TiO <sub>2</sub> r
Titanium dioxide	SkySpring Nanomaterials Inc., P.N.: 7920SCDL	10-30 nm	rutile	APS	TiO <sub>2</sub> rt

Titanium dioxide	SkySpring Nanomaterials Inc., P.N.: 7910DL	10-30 nm	anatase	-	TiO <sub>2a</sub>
zinc-oxid	US Research Nanomaterials Inc., P.N.: US3580	35-45 nm	-	-	ZnO

Table 1. Additives used

### 3.2. Sample preparation

The samples were produced with three different methods based on the same principle. In laboratory conditions, I produced the test specimens by one-pot reaction for the sedimentation and UV resistance tests, and by gravity casting to analyze the use of additives. I used a T-RTM machine to study the effects of production parameters, for warping and reprocessing experiments.

#### One-pot reaction

I divided the monomer required for sample production into two parts, one half of which was added to the initiator and the other half to the activator in 10 ml glass sample holders. After measuring the raw materials, I flushed the sample containers with nitrogen and sealed them airtight. After preparing, the mixtures were dried for 1 hour at 40 °C under a vacuum of 500 mbar. After drying, I let anhydrous nitrogen into the sample bottle. I melted these mixtures in an oven (Despatch LBB2-27-1CE, Despatch Industries GmbH, USA) at 100 °C. After melting, I injected the activator mixture into the initiator mixture using a syringe, then stirred the mixture intensively for half a minute for homogenization, and immediately placed the glass for 5 minutes in an aluminum mold preheated to 150 °C. I then placed the sample holders in cold water to stop the polymerization reaction (quenching), which would have continued without freezing.

I also produced test specimens using another method based on the principle of the same procedure. In the case of the samples containing additives, I first measured the monomer and the activator, and then added the additive in a glass measuring vessel. Then I melted the mixture using a 120 °C heatable magnetic stirring device (Heidolph Hei-Tec GmbH CO. KG, USA) at a speed of 500 rpm and stirred the mixture until it was homogeneous (Figure 1).

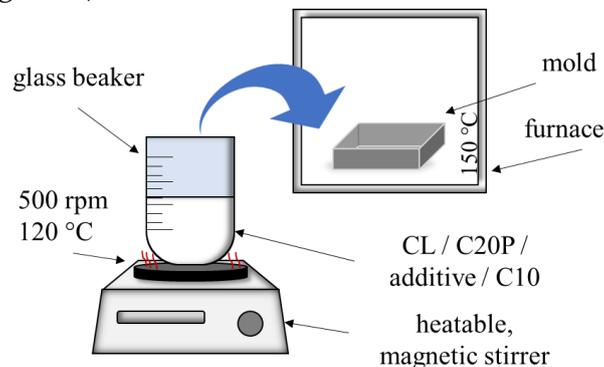


Figure 1. Schematic diagram of the one-pot reaction

Then, I added the appropriate amount of C10 initiator and continued homogenization for another minute. Meanwhile, I heated the tools prepared from aluminum plates to 150 °C in a drying oven (UT20 Heraeus Holding GmbH, Germany), and then poured in the homogeneous mixture of raw materials. Polymerization time was 5 minutes.

### Production of test specimens with the gravity casting machine

To study the possibility of additives, I produced the test specimens by gravity casting, using in situ polymerization. I added the additive to the CL with the activator in it. After that, I placed the CL/C10 and CL/C20P/additive mixtures into the upper two tanks of a stand containing three glass tanks, and before closing them, I flushed the system with nitrogen in order to achieve an inert medium. As the next step, I placed the glass vessel system in an oven (Despatch LBB2-27-1CE, Despatch Industries GmbH, USA) heated to 100 °C to melt the raw materials. I connected a 150 °C mould placed in another oven (UT20 Heraeus Holding GmbH, Germany) to the equipment using silicone pipes. After the melting of the components, they were stirred for 20 s, and I let the melt from the two upper containers into the third (lower) container and then homogenized them with another mixing step. After that, I filled the mould by gravity casting, passing it through a static mixer. After the 10-minute residence (polymerization) time, I stopped the polymerization process by cooling the closed mould in a water bath. Filled and unfilled specimens were produced with a nominal size of 200x260x3 mm. A schematic drawing and a picture of the device is shown in Figure 2, which replicated the manufacturing process of the T-RTM device.

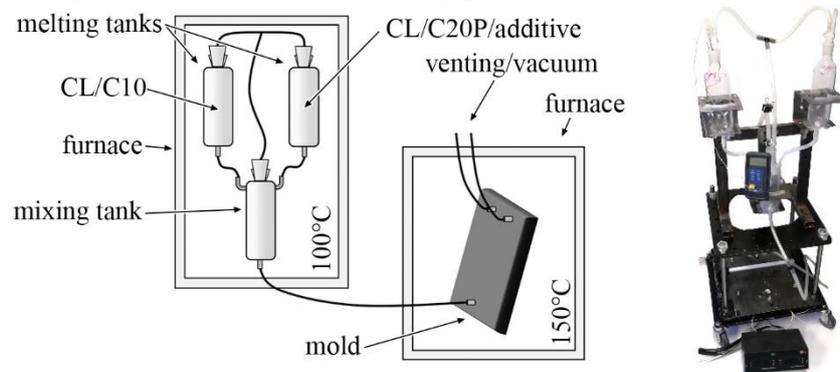


Figure 2. Schematic diagram of the in situ polymerization gravitational casting machine

### Production of test specimens by T-RTM

To analyze the appropriate production parameters, as well as for the adhesion, warping and recyclability tests, I produced samples using the T-RTM technology. I prepared the plate-shaped specimens with a nominal size of 290x510x2-5 mm by in situ polymerization. For this, I used a T-RTM (CFT-FT R.H.13.13.3800.50.0, KraussMaffei Technologies GmbH, Germany) machine and an the experimental mold designed by the BME Department of Polymer Technology and HD Composite Zrt. (Hungary). The machine consists of two dosing units (DU) and a hydraulic press

(Figure 3). The dosing units melt the raw materials, store them in an airtight manner, transport the melted raw materials to the mold carrying press, and inject the preset quantity into the mold. The first dosing unit (DU1) creates the preform, while the second dosing unit (DU2) is suitable for creating the coating. Both operate on the principle of volume displacement. DU1 uses axial piston pumps with an inclined line of action, while DU2 feeds the raw material into the mold using piston pumps. Due to its operating principle, DU1 is not suitable for use of additives, but DU2 is. The function of the hydraulic press is to move the forming mold (opening and closing) and to ensure the required closing force during the process.

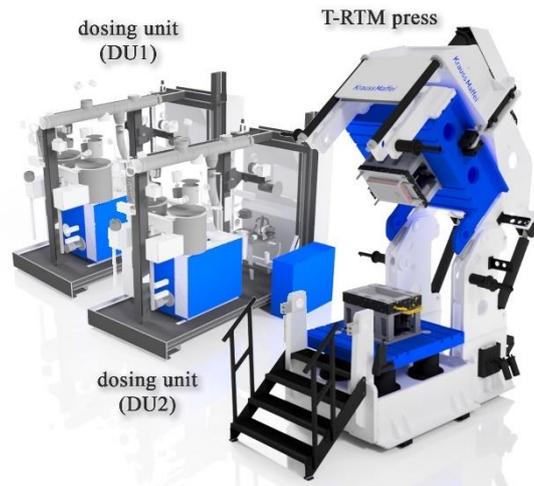


Figure 3. T-RTM unit

As the first step in production, I measured and fed the raw materials in the planned ratio into the dosing unit. I added the additives to DU2, the component that also contained C20P. The activator (CL+C20P (A)) and initiator (CL+C10 (B)) components filled in to the separate melting tanks were melted at 110 °C under a vacuum of 500 mbar. During operation, the melt continuously circulates in a closed system so that it does not come into contact with free air, because of the hydrophilic nature of the raw materials. Figure 4 shows the steps of the production process. Once the raw material is in a molten state, it reaches the mold (1) installed on the press heated up to 150 °C through heatable pipes. The airtight mold cavity has a pressure of less than 1 mbar, in order to ensure the best possible filling (2). The raw materials are fed into the mold cavity with the mixing head. This mixing head, heated to 110 °C, ensures the homogeneous mixing of the components coming from the two separate containers (3). The components only meet each other directly after the mixing head, in order to avoid starting the polymerization process in unwanted places. After the polymerization time (4), the finished product can be removed from the mold (5).

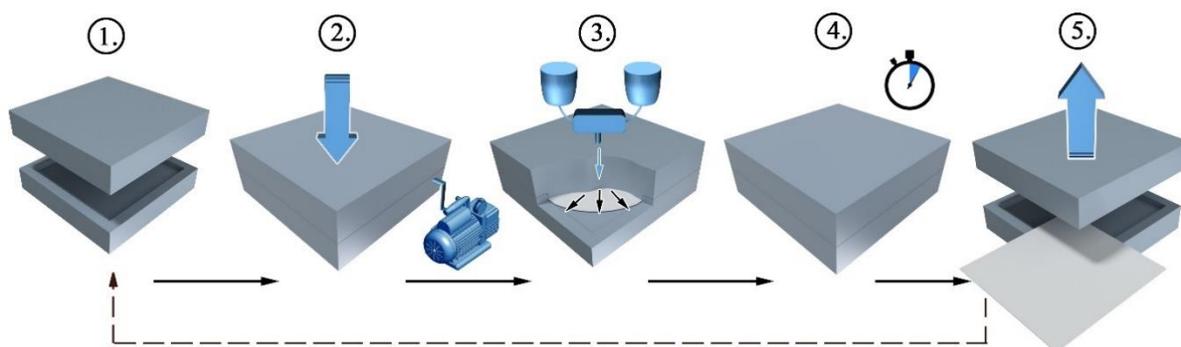


Figure 4: Production cycle diagram 1. preparation of the mold; 2. closing the mold, application of vacuum; 3. filling the cavity; 4. polymerization; 5. opening the mold, removing the product

### 3.3. Characterization of the samples

On the prepared samples, I performed thermal, mechanical, morphological and surface tests. Due to the complex requirements, I used a large number (20 types) of testing methods (Table 2).

Nr.	Test method	Testing equipment	Analysed characteristic	Parameters	Standard nr.
1.	TGA analysis	TGA Q500 (TA Instruments, Inc., USA)	conversion rate	10 °C/min heating/ cooling rate, heating up to 400 °C, 50 ml/min nitrogen gas flow	
2.	DSC analysis	DSC (Q2000, TA Instruments, Inc., USA)	crystalline ratio	25–250 °C range, 10 °C/min heating/cooling rate, 50 ml/min nitrogen gas flow	
3.	Tensile Test	Zwick Z020 (Zwick GmbH & Co. KG, Germany)	tensile strength, tensile modulus	type 5A specimen, 50 mm clamping length, 5 mm/min test speed	MSZ EN ISO 527-2:2012
4.	Bending Test	Zwick Z020 (Zwick GmbH & Co. KG, Germany)	flexural stress at conventional deflection, elongation, tensile modulus	size of specimens: 40x25x2 mm, 32 mm support distance. I did the measurement up to the limit deflection	MSZ EN ISO 178:2019
5.	Charpy Impact Test	Resil Impactor Junior (Ceast S.p.A., Italy)	impact work, ductility index	size of specimens 80x10x5 mm with a 2 mm notch, 62 mm support distance, 2 J hammer, 150° angle covered	MSZ EN ISO 179-2:2020
6.	HDT Test	Ceast HV3 6911.000 (Ceast S.p.A., Italy)	heat deflection temperature	size of specimens 80x10x5 mm, support distance 64 mm, 0.45 MPa stress as load, heating rate 120 °C/hour, permissible deflection 0.34 mm	MSZ EN ISO 75-2:2013
7.	Hardness Test	Zwick Roell H04.3150.000 (Zwick GmbH & Co. KG, Germany)	hardness	specimen thickness 5 mm, Shore D type measuring head	

8.	Optical microscopy	Keyence VHX-5000 (Keyence Corporation, Japan)	size of spherulite	specimen thickness 5 $\mu\text{m}$ , transillumination mode, polarized lenses rotated by 90° relative to each other	-
9.	EDS Test	electron microscope (JEOL JSM 6380LA, Jeol Ltd., Japan)	distribution of additive		
10.	Artificial UV-aging	UV tubes (Sylvania Blacklight 368 nm, Germany)	UV resistance	aging time 2160 hours, 25 RH% humidity, temperature 23 °C, UV tubes: 368 nm wavelength and 39 W/m <sup>2</sup> radiation intensity, specimens were located 40 mm below the UV tubes	
11.	AFM test	AFM - Microscopy) (Nanosurf FlexAFM 5, Nanosurf AG, Switzerland)	Surface topology of UV-treated samples before and after irradiation	analysis with single-beam silicon console, amplitude 2 V, dynamic, probing mode	
12.	FTIR Test	ATR-FTIR (Bruker Tensor II, Bruker Optics Inc., USA)	chemical structure	between 4000 cm <sup>-1</sup> and 400 cm <sup>-1</sup> , resolution 4 cm <sup>-1</sup> , scanning 16 times	
13.	Rheological test	capillary rheometer - Ceast SR 50 (Ceast S.p.A., Italy)	viscosity	capillary length 5 and 20 mm, hole diameter 1 mm, test temperatures 240, 260, 280 °C, shear rates 100–10000 1/s	
14.	Relative solution viscosity	automatic solution viscosity meter - RPV type 1 (PSL Rheotek Ltd., USA)	relative viscosity	Solvent phenol:1,1,2,2-tetrachloroethane 60:40 mixture by weight, solution concentration 0.5 g/dl, test temperature 30 °C	ASTM D460
15.	Adhesive test	PosiTest ATM20A (DeFelsko Corporation, USA)	adhesion	20 mm diameter aluminum specimens	MSZ EN ISO 4624:2016
16.	Warping test	3D scanner - GOM ATOS Core 5M (GOM GmbH, Germany)	warping	analysis with MATLAB	
17.	Moisture absorption test	desiccator	moisture absorption	specimen size 10x30x2 mm, relative humidity 25, 50, 75, 100 RH%, in water, temperature 23 °C, measurement time interval 3 days	

18.	Shrinkage test	caliper	shrinkage	the difference between the actual inclusion dimensions of specimen and the dimensions of the mold used for production	
19.	Sedimentation test	camera, Photoshop / TGA	sedimentation of additive in CL	72 dpi resolution, definition of 3 points: top of caprolactam system, bottom of test tube, top of settled part	procedure I developed myself
20.	Color test	Color-Guide Sphere 6834 (BYK-Gardner GmbH, Germany)	yellowing	average of 3 point measurements per sample, D65 type illumination, 10° field of view	

Table 1 Summary of tests

## 4. SUMMARY

Nowadays, thanks to the rapid development of the automotive industry, military industry, and sports goods production, the stricter regulations for the sector and the growing expectations for the characteristics of the products, more and more thermoplastic matrix composites are used in the production of technical parts. During the production of composites with a reinforcing fabric, the wide range of thermoplastics is limited by their high viscosity in the molten state. The solution to this problem can be CL, from which PA 6 can be produced by anionic ring-opening in situ polymerization. In order to fulfil the requirements for the product's complex properties, the use of additives and fillers is necessary, which can be filtered out by the reinforcing fabric, thereby leading to inhomogeneity in the final product. In order to eliminate this, it may be necessary to create a coating layer. One of the most suitable processes for the in situ production of PA 6 from CL, which can also be used in industrial conditions, is the T-RTM technology. Due to the novelty of the technology, this is an area that is currently under-researched, although research is becoming increasingly intensive.

Based on the review of the literature, I came to the conclusion that the researches mostly focused on polyamides produced under laboratory conditions, and the industrial technology of T-RTM was used by very few people. The main result of my literature research is that the best initiator-activator combination with CL is C10-C20P, and that it is necessary to ensure a moisture-free environment during production. The optimal mold temperature is 150 °C, where in the case of 3 m/m% C10 and 3 m/m% C20P, the conversion rate is over 99% and a high crystalline fraction can be achieved with a polymerization time of 5 minutes, but this has only been verified on samples produced under laboratory conditions. The investigation and modeling of the moisture absorption capacity of PA 6 products manufactured with T-RTM technology in different humidity and aqueous environments is still little researched. In order to increase the value and achieve the expected properties, we need to use different additives. In polymers, titanium dioxide is often used to increase UV resistance, but its addition to CL and the properties and UV resistance of the TiO<sub>2</sub>/PA6 composite created by in situ polymerization have not been investigated so far. The application of solid-phase, granular additives is limited because they are filtered through the reinforcing fabric, so it is necessary to create a coating layer—it is possible in the so-called in-mold coating (IMC) procedure. To my knowledge, the IMC process has not yet been used by any research group in combination with T-RTM technology, during which both the preform and the matrix material of the coating layer was PA 6. During my research, I aimed to develop this procedure and rectify the above-mentioned deficiencies.

As the first step (Figure 5), I investigated the effect of the production parameters of T-RTM on the crystalline fraction, degree of conversion, water absorption, and morphological and mechanical properties of PA 6. I found that increasing mold temperature decreases the crystalline fraction and the degree of conversion, as a result

of which the hardness, ultimate bending stress, bending modulus and heat resistance of the samples decrease, but their specific impact work and water absorption capacity increase. Based on the results of these measurements, I selected the most suitable production setting (mold temperature of 150 °C and a residence time of 3 minutes), which I used during further experiments.

As a next step, I examined the effect of additives added to the caprolactam system based on the results of the sedimentation tests. In doing so, I used different types, sizes and amounts of additives. I also examined the degree of conversion and crystalline fraction of the samples in order to study their effect on the polymerization process. I came to the conclusion that lowest sedimentation can be achieved with nanosized titanium dioxide with silane surface treatment. TiO<sub>2</sub> acts as a nucleating agent on PA 6 up to a certain amount (0.6 m/m%), but above that, it inhibits the crystallization process and the movement of molecular chains during polymerization, which can have a negative effect on the structure and properties of the polyamide.

After that, I used different amounts of nano-sized, silane-coated and uncoated titanium dioxide in producing specimens. I studied and modelled their moisture absorption capacity with different humidity levels and when they were immersed in aqueous media. In the aqueous medium, the moisture content of the samples first increased and then decreased over time. This is caused by the accelerated diffusion of the remaining monomer content of the samples. Using the results of the test, I created a complex model that can be used to measure the moisture content of PA 6 samples under water.

I then studied the effect of additives on the UV resistance of PA 6. Based on the results, I came to the conclusion that there is also a titanium dioxide quantity limit (0.6 m/m%), above which degradation occurs on the surface of the samples. The explanation for this is that the UV filter effect of nanosized TiO<sub>2</sub> can no longer compensate for its photocatalytic effect. Furthermore, the increased content of additives forces the high-energy UV rays closer to the surface, where they are thus more concentrated, increasing degradation.

I have successfully developed the surface coating process during which the coating layer, also PA 6 with a filler, can be created in one production cycle on the PA 6 preform produced from CL by anionic ring-opening in situ polymerization, by T-RTM. I studied the adhesion between the base layer of the complex product produced in this way and the coating layer injected on it, as well as the effect of the deformation resulting from the different shrinkage of the two layers. The resulting adhesion was adequate if, during production, the preform did not come in contact with ambient moisture before the coating layer was injected. A worse adhesive bond can be achieved with the preform created with a shorter production time than with a production time of 180 s. In this way, a system with higher adhesive strength can be created than by commonly used painting. The results of the warping test showed that the thicker coating layer had a greater influence on the shrinkage irregularities of the preform, and that the additive had no significant effect.

Finally, I examined the recyclability of cast PA 6 samples by injection molding, without the use of additives. The experiments proved to be successful, so PA 6 produced by T-RTM can be reprocessed by injection molding up to a processing temperature of 250 °C. I compared the thermal, morphological and mechanical properties of samples molded with the T-RTM technology, those molded by T-RTM followed by re-injection, and those molded from the polycondensation base material. The samples produced by T-RTM had a higher crystalline fraction and a higher relative solution viscosity, and this was also reflected in the mechanical properties.

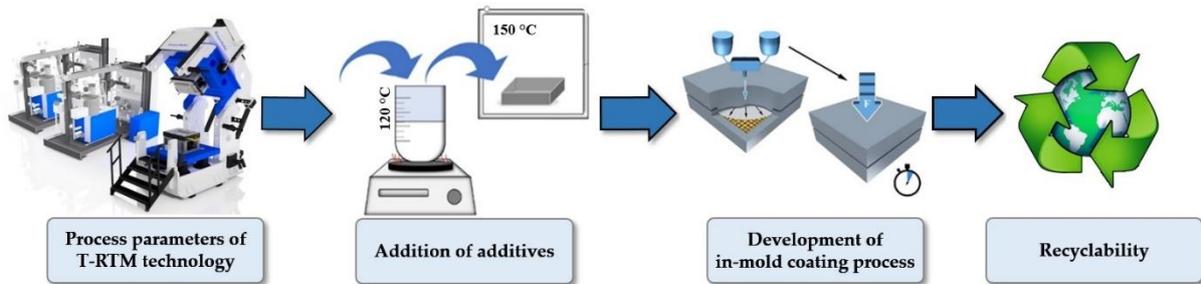


Figure 5. Progress of my research

## 4.1. Theses

### THESIS 1

The surface hardness, ultimate bending stress, and bending modulus of polyamide 6, produced by anionic ring-opening polymerization from  $\epsilon$ -caprolactam with T-RTM technology decrease, and its impact resistance increases as the applied mold temperature increases. The reason for this is that with increasing mold temperature, a smaller crystalline fraction is formed, the effect of which on the static and quasi-static mechanical properties cannot be compensated for by the increase in molecular weight. In the case of dynamic tests, molecular weight is the key factor affecting the properties of PA 6. I proved my statement with thermal, morphological and mechanical tests on polyamide 6 samples produced with T-RTM technology in the typical polymerization temperature range (150–175 °C), produced from  $\epsilon$ -caprolactam (AP-NYLON), initiator (Bruggolen C10) and activator (Bruggolen C20P). [1, 2]

### THESIS 2

The mass change measured during the moisture absorption of polyamide 6 produced by anionic ring-opening polymerization can be described with the following equation:

$$m_e(t) = m(t) - m_m(t)$$

where  $m_e(t)$  is the mass change of the sample [g],  $m(t)$  is the increase in mass measured at a given moment of the water absorption of the sample compared to the weight of the sample before water absorption [g], and  $m_m(t)$  is the amount of monomer dissolving as a function of time [g].  $m(t)$  is the explicit version of the mass-based liquid absorption model defined by Vas and Nagy:

$$m(t) = m_{\infty} \cdot \left[ 1 - e^{-\left(\frac{2 \cdot c \cdot t}{m_{\infty}}\right)^k} \right]^{\frac{1}{2 \cdot k}}$$

where  $m_{\infty}$  is the equilibrium moisture content of the sample [g],  $t$  is the time of water absorption [h],  $c$  is a constant [g/h] and  $k=3/2$ . I proved with measurements that the constant characterizing the rate of moisture absorption  $c$  depends on the crystalline fraction of the polymer, ambient humidity, and the content and type of the additive.

And  $m_m(t)$  can be described with an Avrami-type relation:

$$m_m(t) = m_{m\infty} \cdot (1 - e^{-f \cdot t})^{c_m}$$

where  $m_m(t)$  is the amount of monomer dissolving as a function of time [g],  $m_{m\infty}$  is the monomer content of the sample determined by TGA measurement [g],  $f$  is the parameter fitted to the data [1/h],  $t$  is the elapsed time [h], and  $c_m$  is a data fitting constant [-]. Due to the slow diffusion of the monomer at different atmospheric humidity levels, the  $m_m(t)$  term is negligible, but it accelerates diffusion in the sample submerged in water, so it must be taken into account. My statement on polyamide 6 samples produced from  $\epsilon$ -caprolactam (AP-NYLON), initiator (Bruggolen C10) and activator (Bruggolen C20P), unfilled and filled with titanium dioxide, in mediums with different humidity (25, 50, 75, 100 RH%) and placed under water, was proved with tests carried out at the ambient temperature of 23 °C. [3]

### THESIS 3

The UV resistance of the surface of polyamide 6 samples produced by anionic ring-opening polymerization from  $\epsilon$ -caprolactam can be improved by adding a maximum of 0.6 m/m% nanosized titanium dioxide, but above that, significant surface degradation occurs due to UV radiation. The explanation for this is that the light reflection of nanosized TiO<sub>2</sub> can no longer compensate for the photocatalytic effect of the additive. Furthermore, the increased amount of additives does not allow high-energy UV rays to penetrate deeper into the material, so they are more concentrated near the surface, increasing degradation. I proved my statement by studying the crystalline proportion and the colour of the samples, and AFM and FTIR analysis. For my tests, I produced silane-treated and untreated PA 6 from  $\epsilon$ -caprolactam (AP-NYLON), initiator (Bruggolen C10) and activator (Bruggolen C20P), with 30 nm TiO<sub>2</sub> as additive. [4-6]

### THESIS 4

a) I developed a surface coating process for the T-RTM technology, during which a coating layer can be created on the surface of the product with the same raw materials in the same technological cycle. After the production of the preform, the monomer mixture of the surface layer can be injected when the mold is partially opened, and polymerized by pressing. During the partial opening of the sealed mold, the preform cannot come into contact with the atmosphere, because its moisture content prevents the adhesion between the preform and the surface layer. I proved the applicability of

the method to a polyamide 6-based preform made from  $\epsilon$ -caprolactam (AP-NYLON), initiator (Bruggolen C10) and activator (Bruggolen C20P), injecting a coating layer also based on  $\epsilon$ -caprolactam.

b) The adhesion between the preform and the surface layer can be improved by increasing the residence time of the preform. If the coating layer with a lower temperature (110 °C) is injected before the polymerization process of the preform is complete, it freezes the polymerization reaction taking place on the surface, thereby lowering the quality of the adhesion between the two layers. I proved my statement with adhesion tests on polyamide 6 samples produced from  $\epsilon$ -caprolactam (AP-NYLON), initiator (Bruggolen C10) and activator (Bruggolen C20P) by T-RTM, with a residence time of 70, 120 and 180 s. [2, 7, 8, 10]

## THESIS 5

Polyamide 6 products produced from  $\epsilon$ -caprolactam by T-RTM by anionic ring-opening polymerization can be reprocessed by injection molding, without the use of additives or auxiliary materials, but they degrade significantly during reprocessing. The crystalline proportion, molecular weight, and mechanical properties of the reprocessed products are similar to the product molded from the polyamide 6 raw material produced by polycondensation. I proved my claim with thermal, rheological and mechanical tests on samples made from  $\epsilon$ -caprolactam (AP-NYLON), initiator (Bruggolen C10) and activator (Bruggolen C20P), produced by T-RTM, mechanically recycled and then injection molded samples, and samples injection molded from B30S (Durethan) polycondensation PA 6 [9, 11]

## 5. PUBLICATIONS SUPPORTING THE THESIS POINTS

- 1 **Semperger O. V.**, Suplicz A.: The effect of the parameters of T-RTM on the properties of polyamide 6 prepared by in-situ polymerization. *Materials*, **13**, 4-15 (2020).
- 2 **Semperger O.**, Óri Z., Hegedűs G., Molnár P.: Gyártástechnológiai fejlesztés nagy komplexitású. hőre lágyuló mátrixú kompozit előállítására. *Polimerek*, **4**, 123-128 (2018).
- 3 **Semperger O. V.**, Suplicz A.: The effect of titanium dioxide on the moisture absorption of polyamide 6 prepared by T-RTM. Institute of Physics (IOP) Conference Series: Materials Science and Engineering, **903**, 012009 (2020).
- 4 **Semperger O. V.**, Suplicz A.: Titán-dioxid hatása az in-situ polimerizációval előállított poliamid 6 minták tulajdonságaira. *Polimerek*, **11**, 730-733 (2019).
- 5 **Semperger O. V.**, Suplicz A.: Titán-dioxid hatása az in-situ polimerizációval előállított poliamid 6 minták tulajdonságaira. in 'XXVII. Nemzetközi Gépészeti Konferencia. Nagyvárad, Románia', 472-475 (2019).
- 6 **Semperger O. V.**, Osváth Zs., Pásztor Sz., Suplicz A.: The effect of the titanium dioxide nanoparticles on the morphology and degradation of polyamide 6 prepared by anionic ring-opening polymerization. *Polymer Engineering and Science*, **62**, 2079-2088 (2022).
- 7 **Semperger O. V.**, Pomlényi P., Suplicz A.: Felület-bevonatolási eljárás T-RTM technológiához. *Polimerek*, **6**, 186-192 (2021).
- 8 Suplicz A., Boros R., **Semperger O. V.**: Investigation of the interfacial adhesion of glass bead-filled multicomponent injection moulded composites. Institute of Physics (IOP) Conference Series: Materials Science and Engineering, **903**, 012049 (2020).
- 9 Suplicz A., **Semperger O. V.**, Kovács J. G.: Modeling the thermal conductivity inhomogeneities of injection molded particle-filled composites, caused by segregation. *Polymers*, **11**, 1691-1703 (2019).
- 10 **Semperger O. V.**, Török D., Suplicz A.: Development and analysis of an in-mold coating procedure for Thermoplastic Resin Transfer Molding to produce PA6 composites with a multifunctional surface. *Periodica Polytechnica, Mechanical Engineering*, (2022).
- 11 **Semperger O. V.**, Suplicz A.: Sustainability in Thermoplastic Resin Transfer Molding technology: recyclability of polyamide 6 produced by anionic ring-opening polymerization of  $\epsilon$ -caprolactam. *Materials Today Communications*, (2022) – under review