Process Development for Ultra-Thin Fiber-Reinforced Thermoplastic Backplates for Foldable Display Applications

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1. Abstract

The development of ultra-thin composite backplates for foldable display applications requires a balance between processability and material performance. This study investigated the influence of binder material or tackifier of the anionic polymerization of polyamide 6 (aPA6) used for ultra-thin composite backplates. Different powder binders were tested on their influence on the reaction kinetic of ε-caprolactam to aPA6. Two of the four materials studied showed a negative impact on the exothermic temperature rise during the reaction. Carbon fiber sheets (CF aPA6 sheets) were manufactured with different binder proportions of a polyamide 12 (PA12) binder in the Thermoplastic Resin Transfer Molding Process (T-RTM). At higher binder content the permeability of the preforms is decreasing. The properties of CF PA6 sheets were investigated as a function of the binder content. As the binder content increases, the residual monomer content rises, while the weight-average molecular weight decreases. No trend on crystallization could be detected.

2. Introduction

Today, industries are evolving faster than ever before. In addition to the automotive and aerospace industries, the electronics industry is also showing a growing interest in lightweight construction solutions and, consequently, in the use of composite materials [1]. Foldable display devices in particular require ultra-thin backplate structures combining low thickness, high stiffness and sufficient flexibility under cyclic bending. In the electronics industry, a high degree of automation and fast production cycles are essential. Mostly thin-walled, filigree parts (≤ 250 µm) need to be impregnated. Moreover, from a end of life perspective, thermoplastic matrices are of interest due to recycling potential.

One option is to use a thermoplastic matrix which can be obtained through the polymerization of low-viscosity monomers, such as ε-caprolactam. This monomer has a low viscosity of 3 - 5 mPas (at 100 °C) [2] and reacts in situ via activated anionic ring-opening polymerization (AAROP) to anionically polymerized Polyamide 6 (aPA6) [2]. It is used in the thermoplastic resin transfer

molding process (T-RTM) as well as in thermoplastic pultrusion [3,4]. The T-RTM process is an injection process in which a dry preform is impregnated with a matrix consisting of a monomer, an activator, and a catalyst, and then polymerized in-situ under pressure and temperature [5]. Due to the low polymerization temperature, a high degree of crystallization occurs, which has a positive effect on its mechanical properties [6,7]. This process is especially suitable for foldable backplates due to its ability to impregnate dry fiber preforms with low-viscosity monomers and produce ultra-thin laminates in short cycle times; however, process control becomes increasingly critical at very low thicknesses.

Understanding and controlling the T-RTM process for such thin laminates and their parameters remains a challenge, as there are process steps occurring simultaneously. The rate of polymerization can be influenced by the proportion of activator and catalyst [8]. The mold temperature has a significant influence on polymerization and crystallization conditions [9]. Next to the process parameters, also interferences such as fibers or fillers that influence the polymerization must be understood in detail. The influence of water and fiber sizing has already been studied before [10,11].

The influence of binder or tackifier on the polymerization properties of ε-caprolactam has not been studied yet. These are often applied to stabilize the preforms during lamination and impregnation. Commonly used binder materials are powder binders [12]. They are applied on the surface of the preform by a scattering process, then liquefied by heat, and after the cooling process due to the solidification of the binder, the adjoin fibers bond together [13,14]. The binder used affects the behavior of the preform throughout the entire manufacturing process. Increasing the binder content will also increase the initial thickness of the preform, which will result in an increase of compression stroke and time [15]. Moreover, the binder content has a significant influence on the permeability of the preform. Studies showed that a binder applied on the surface of the fabric leads to reduced permeability as the binder content increases [14,16]. A binder migration and an inhomogeneous dissolution of the binder material during the infiltration process can result in varying binder concentrations throughout the preform. This will result in inhomogeneous polymerization, which has an influence on quality parameters such as inhomogeneous shrinkage, inhomogeneous mechanical properties, and thermally induced stresses in the final part [13]. In addition to the influence of the binder system's concentration, the chemical compatibility of the binder system with the matrix system being used is also relevant. Lee et al. and Terekhov et al. recommend selecting a binder based on the same structural formulation as the matrix to be impregnated [14,12].

This study investigates the influence of binder systems on the polymerization behavior of ε-caprolactam. First, different binder materials have been investigated for their compatibility with ε-caprolactam. The influence of one appropriate binder material with different proportions on the processing properties in the T-RTM process, as well as on the polymerization properties, is investigated. The aim is to identify a binder compatible with ε-caprolactam for preform production and its use in the T-RTM process for the manufacturing of ultra-thin composite backplates.

3. Experiments

3.1. Materials

In this study, Griltex D 1428A (PA12) and Griltex D 1796A (Polyamide 6 (PA6)), both from EMS Chemie Holding AG, Rilsan ROTO 11 Natural (Polymaide 11 (PA11)) (Arkema GmbH), and CeTePox® AM XP 182-3 (CTP Advanced Materials GmbH) are investigated as binder materials. The binder materials must be powder binder, compatible with the ε-caprolactam reaction and the preform manufacturing process. As matrix material ε-caprolactam (AP-Nylon Caprolactam Flakes), Activator (BRUGGOLEN C20P), and Catalyst (BRUGGOLEN C10), all from Brüggemann Chemical, were used. Carbon fiber (CF) material T700SC-1200-60E-P1 from Toray Carbon Fibers Europe S.A was used.

3.2. Preparation of the Compatibility Test

Compatibility of different binder materials with anionic polymerization was investigated in laboratory tests. A low-pressure injection and dosing unit from ATP Kunststofftechnik AG (Switzerland) were used. ε-caprolactam with mass fraction (w) w = 2 % BRUGGOLEN C20P were stored in one vessel ε-caprolactam and w = 4 % BRUGGOLEN C10 were stored in the other vessel. The vessels and the mixing head were heated to 150 °C under nitrogen. Temperature sensors (Thermoelement Typ K) were installed inside the beaker to measure the exothermic temperature rise during the polymerization. The mixed material was injected at a ratio of 1:1 into a beaker heated in an oil bath to 152 °C. A binder content of w = 13 % was applied to the CF beforehand. A fiber volume fraction (FVF) of FVF = 10 % was selected for the beaker test. The flow rate was 50 cm^3/s and the polymerization time was 180 s.

3.3. Preparation of the Preform Material

Preform material was produced in three process steps. First, the carbon fiber rovings are spread into tows with a width of 14 mm on an industrial fiber spreading system (M&A Dieterle GmbH). The binder system was applied by an automatic scattering system and fixed by heating at 150 °C. The proportion of binder material was varied from w = 5 % to 15 % in steps of 5 %. Preform material was produced by a crosslayer process. The size of the preform material was 895 x 545 mm^2 with a $(0)_2$ layup. The preform material was dried before at 80 °C for 72 h.

3.4. Preparation of the CF aPA6 plates

The CF reinforced aPA6 sheets with a dimension of 895 x 545 x 0,25 mm^3 were produced by the T-RTM process. The trials were conducted with a Dieffenbacher DYL 630/500 hydraulic upper barrel press with parallel control and a low-pressure injection and dosing unit from ATP Kunststofftechnik AG (Schwitzerland) (see Figure 1). The mold temperature was 150 °C, and the matrix was stored at 110 °C in the dosing unit. The proportion of the reactive components was w = 3 % BRUGGOLEN CP10 and w = 1.5 % BRUGGOLEN C20P (mixing ratio of 1:1). Before the injection the mold was evacuated. The output rate ($\dot{v}$) varied from $\dot{v}$ = 6 cm^3/s to $\dot{v}$ = 12 cm^3/s till $\dot{v}$ = 18 cm^3/s. During the injection, a press force of 200 kN was built up for 77.5 s, 52.5 s, and 44.17 s. After the injection, a press force of 3000 kN was built up for 240 s. Pressure sensors Typ 6161A (Kistler Instrumente AG) were installed in the cavity to record the pressure profile during

the process. Three CF aPA6 sheets were produced of w = 10 % and w = 15% binder material and matrix output rate. In addition, one CF aPA6 sheet was produced using w = 5 % binder material at an output rate of $\dot{v}$ = 6 cm^3/s and $\dot{v}$ = 18 cm^3/s.

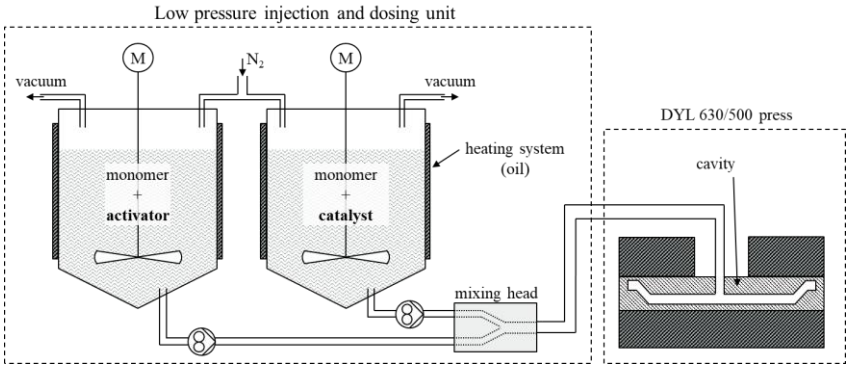

Figure 1: Process scheme of thermoplastic Resin Transfer Molding. According to [2]

3.5. Characterization

Thickness measuring of the CF aPA6 sheets: Three measurements were taken at each position using a measuring gauge according to the positions shown in Figure 2.

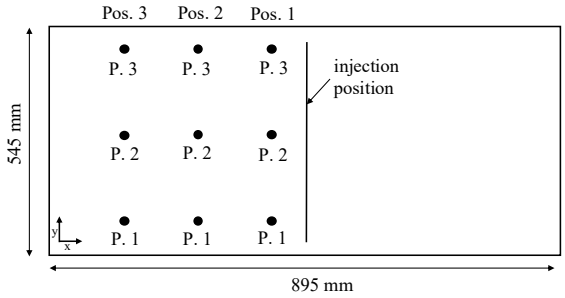

Figure 2: Thickness measuring points in the CF aPA6 sheet

Reversed Phase High Performance Liquid Chromatography (RP-HPLC): This was conducted using an Agilent 1100 series chromatograph, with a sample volume of 5 µl and a flow rate of 0.6 cm^3/min. The eluent consisted of 15 % acetonitrile and water. Using a Soxhlet extraction with demineralized, high-purity water, the ε-caprolactam concentration was extracted after 6.5 hours.

Gel permeation chromatography (GPC): In an LCI 100 chromatograph, the sample was dissolved in hexafluoroisopropanol (HFIP) at a concentration of 1.0 to 1.5 mg/cm^3. After a 24-hour holding time, the data were collected using a concentration-dependent RI detector (Agilent 1100 Refractive Index Detector) at a temperature of 35 °C and a flow rate of 1.0 ml/min.

Differential scanning calorimetry (DSC): A Caliris 300 Select from NETZSCH GmbH was used. 2 mg of matrix material was heated up at 10 K/min to 250 °C, cooled down to 0 °C, and then heated up to 250 °C. The test was conducted under an inert atmosphere.

4. Results

4.1. Compatibility with ε-caprolactam

Table 1 shows 4 different binder materials that were investigated for the use of preform material for the T-RTM process.

Table 1: Results of the compatibility test of different binder materials with ε-caprolactam

No	binder material	Polymerizable	Preform manufacturing possible
1	Griltex D 1796A	Indicates impairment	Yes
2	CeTePox AM XP 182-3	Indicates impairment	*-
3	Griltex D 1428A	Yes	Yes
4	Rilsan Roto 11	Yes	No

*Further testing was not conducted since this is an epoxy binder

Of the four binder materials analyzed, two did not interfere with the polymerization process. Griltex D 1796A and CeTePox AM XP 182-3 exhibited the lowest temperature rise during polymerization. Because of the linear connection between the exothermic temperature rise and the polymerization gradient, this is a good indicator for the polymerization [17]. The epoxy binder (CeTePox AM XP 182-3) contains a large number of free epoxy groups [18]. Due to the high nucleophilicity of the epoxy group, the anion in the activator and catalyst react with it [19]. As a result, the activator for the AAROP of ε-caprolactam is no longer available, therefore the reaction is aborted. Due to the similar chemical structures of Griltex D 1428 A (PA12) and Rilsan Roto 11 (PA11) compared to aPA6, these exhibited the highest temperature rise during polymerization. Preform manufacturing was possible using the Griltex D 1428 A and the Griltex D 1796 A binders. Due to the particle size of the Rilsan Roto 11 material, it was not possible to process it using the crosslayer.

Consequently, Griltex D 1428A was selected for further investigation.

4.2. Influence of the binder on the impregnation behavior

The effect of the binder on impregnation behavior was investigated at three different proportions (w = 5 %, w = 10 %, and w = 15 %). The thickness of the CF aPA6 sheets was measured after polymerization and is shown in Figure 3.

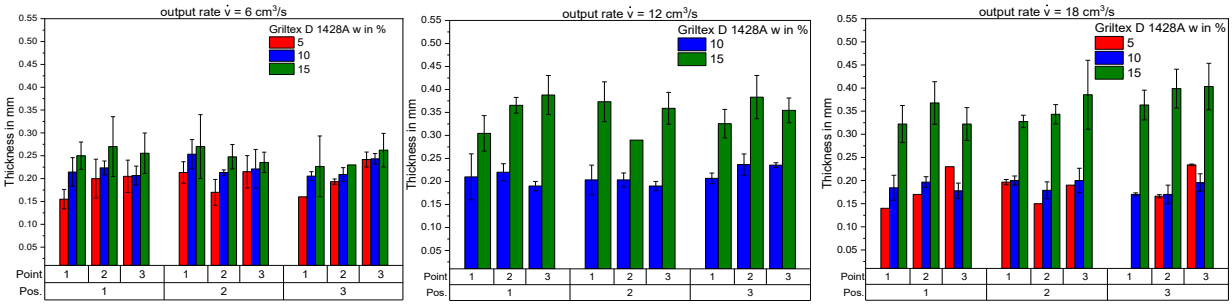

Figure 3. Thickness measuring at 3 different points according to Figure 2

The lowest thickness of the CRF aPA6 sheets was measured for w = 5 % Griltex D 1428A and an output rate of $\dot{v}$ = 6 cm³/s at measuring Pos. 1 Point 1 with 0.155 mm. At Pos. 1 Point 3 the sample with w = 15 % binder material and an output rate of $\dot{v}$ = 12 cm³/s shows the highest thickness

(0.388 mm). With a higher binder content, the thickness of the CF aPA6 sheets increases. As the output rate increases, the difference in thickness per binder proportion also increases.

The influence of the binder material on permeability is shown in the pressure data. Figure 4 shows the pressure in the cavity on the injection point with w = 10 % and w = 15 % Griltex D 1428 A at the output rate of a) $\dot{v}$ = 12 cm^3/s (left side) and b) $\dot{v}$ = 18 cm^3/s (right side).

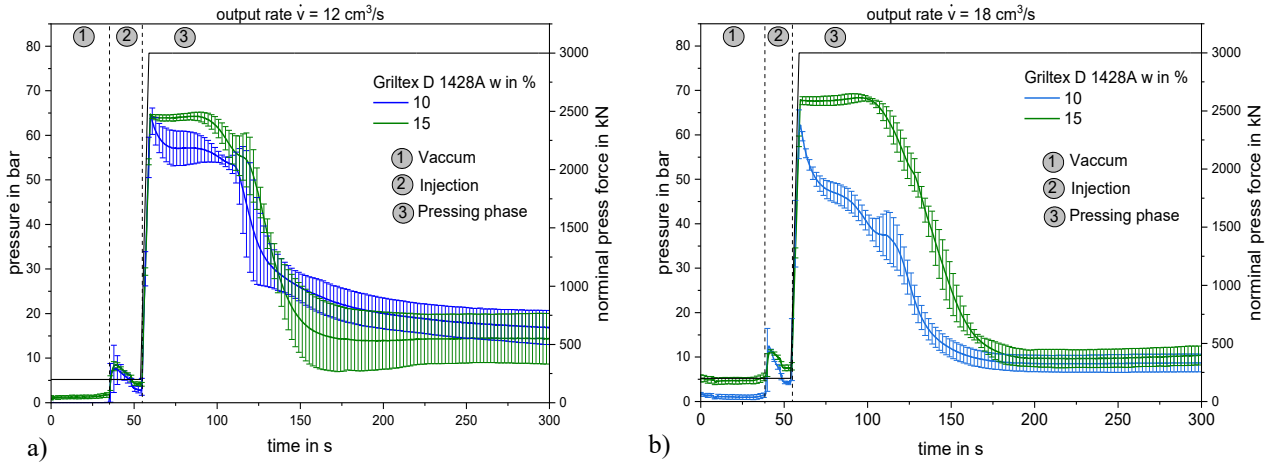

Figure 4. Pressure curve of the matrix material measured at the injection point with an output rate of $\dot{v}$ = 12 cm3/s (a) and $\dot{v}$ = 18 cm3/s (b)

During the injection phase, the pressure rises slightly for all samples and then drops. Due to the different output rate, the time of injection will differ. The start of the pressing phase can be seen from the sharp rise in pressure starting at 54 s for all samples. For the samples with w = 15 % binder content, a pressure plateau can be seen. The pressure plateau for the sample with w = 10 % and an output rate of $\dot{v}$ = 12 cm^3/s is lower and shorter. At an output rate of $\dot{v}$ = 18 cm^3/s, no plateau is observable in the sample with w = 10 % Griltex D 1428A.

Increasing the binder material leads to a reduction in the permeability of the preform material, which makes it more difficult for the matrix to infiltrate the preform. As a result, the thickness of the CF aPA6 sheets increases, and a plateau during the T-RTM process can be seen. The binder material on the preform surface blocks the flow channels between the fiber bundles, thereby hindering the interlaminar matrix flow. Similar phenomena have already been demonstrated by Estrada et al. and Shih et al. [20,16]. The formation of a pressure plateau by increasing the binder proportion during the process is based on Darcy's law. Under identical process conditions, a high pressure drop at w = 10 % leads to a high matrix flow through the preform, while the formation of a pressure plateau at w = 15 % indicated a low matrix flow. The study of Rohatgi et al showed a similar effect [14].

4.3. Influence of the binder material on the material properties of aPA6

The residual monomer content (RMC) of ε-caprolactam was analyzed for all samples. The results are shown in Figure 5.

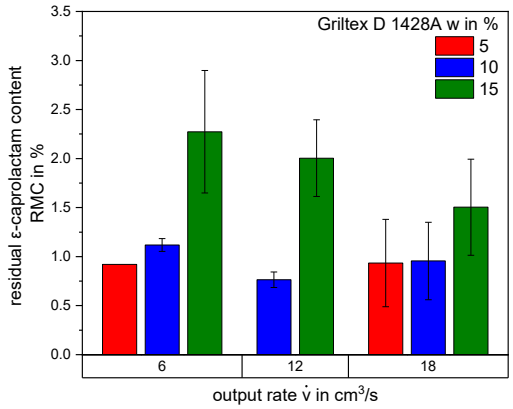

Figure 5. Residual monomer content of CF aPA6 sheets. Analyzed by HPLC. w = 5 % and $\dot{v}$ = 6 cm3/s refer to a single measurement

The ε-caprolactam content rises from w = 5 % to w = 15 % Griltex D 1428A. This phenomenon is observed independently of the output rate. With increasing output rate, the RMC decreases for w = 15 % Griltex D 1428A.

The influence of the binder content on the weight-average molecular mass M_w is noticeable. The results are shown in Figure 6.

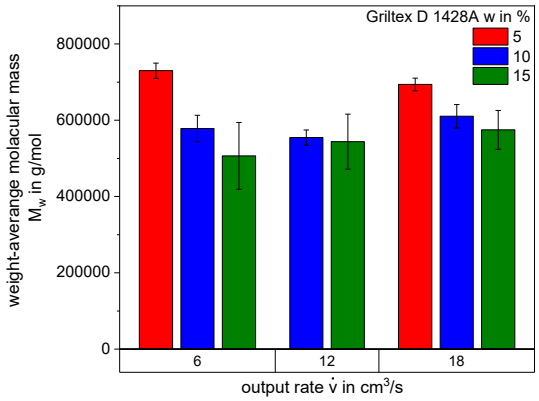

Figure 6. Weight-average molecular mass of CFaPA6 plates at different binder proportions. Analyzed by GPC

As the binder content increases, M_w decreases at an output rate of $\dot{v} = 6$ cm^3/s. However, the standard deviations overlap; this is also noticeable at an output rate of $\dot{v} = 12$ cm^3/s and $\dot{v} = 18$ cm^3/s. In contrast to the decreasing of M_w the standard deviation of the value is increasing proportionally to the binder content.

It can be assumed that PA12 acts as an adsorbent for ε-caprolactam. Adsorption often occurs at the interface between a fluid phase and a condensing phase [21]. PA12 occurs in the form of solid particles and therefore exhibits stationary behavior. The aPA6 chain growing from the liquid is dynamic and does not provide a stable platform for the ε-caprolactam monomers. The amide group (O=C-N-H) in the ε-caprolactam forms a hydrogen bond with the carbonyl group (C=O) in the PA12, which leads to a reduction in the monomer concentration. As a result of the adsorption onto

the PA12 particles, the monomer is no longer accessible for polymerization within the intended time frame in the mold. This phenomenon can also induce shorter chains as the amount of monomer per polymer chain growth is reduced. The adsorption behavior of polar substances on the surface of PA12 has already been demonstrated by Han et al. [22] and Aldahash et al. [23] in separate studies. In addition, the standard deviation, which is inversely proportional to the weight-average molecular mass, can indicate a higher degree of branching points at higher binder contents. The activator can deblock at temperatures between 140 °C – 160 °C at the beginning of the polymerization, building hexamethylene diisocyanate. These can form crosslinking points with the amide groups of the aPA6 and PA12 polymer. Due to the small number of aPA6 polymer chains at the start of the reaction, a branching point may form with a PA12 molecule. This reduces the chain length and increases the standard deviation and the increase in RMC.

4.4. Influence of the binder material on the degree of crystallinity (X_c)

The influence of the binder material on the degree of crystallinity (X_c) was analyzed by DSC. The results are shown in Figure 7.

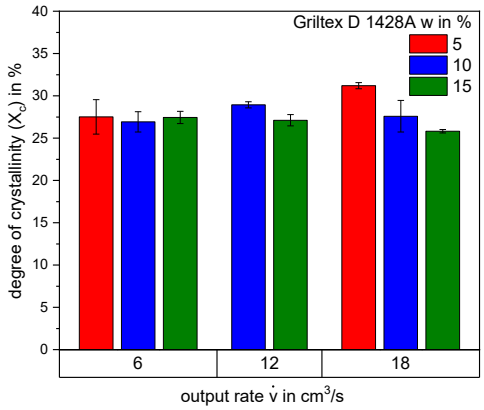

Figure 7: Degree of crystallinity (Xc) of CFaPA6 sheets at different binder proportions. Analyzed by DSC

The binder shows a slight influence on the degree of crystallinity of ε-caprolactam during the polymerization. At an output rate of $\dot{v} = 6$ cm^3/s there is no detectable influence of the binder noticeable. At higher output rates of $\dot{v} = 12$ cm^3/s and $\dot{v} = 18$ cm^3/s the degree of crystallinity is decreasing as the binder content is increasing. The crystallization process depends on the number of polymer chains available during the polymerization [24]. Since this number decreases as the binder content increases (see Fig. 6), this could lead to a reduction in crystallization. On the other hand, it can be assumed that the PA12 molecules act as nucleation from which chain growth can occur [7].

5. Conclusion

In this work, the influence of the binder material Griltex D 1428A on the impregnation behavior, the residual monomer content (RMC) of ε-caprolactam, the weight-average molecular mass, and the degree of crystallinity (X_c) was investigated. The proportion of the binder material has a

significant influence on the permeability of the preform. With increasing binder content, the permeability of the preform decreases. The residual monomer content and the weight-average molar mass were decreasing as the binder content increased. This might be due to the adsorption behavior of the PA12 molecules and the formation of crosslinking points during the polymerization process of ε-caprolactam. The residual monomer content and the weight-average molar mass are important parameters for evaluating the quality of aPA6. This highlights a critical trade-off between preform stability and permeability in the processing of ultra-thin laminates. The investigation of the binder material on the degree of crystallinity does not show a clear trend. This must be investigated further.

Acknowledgment

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