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The effect of titanium dioxide on the moisture absorption of polyamide 6 prepared by T-RTM

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Abstract. In recent years, the replacement of metal components with composites is becoming more and more common in the automotive industry. Thermoplastic composites are recyclable, which meets requirements. Impregnating the reinforcing material is difficult but caprolactam is a good choice because in melt state, it has similar viscosity to that of water. Polyamide 6 can be produced from caprolactam by ring opening in-situ polymerisation. We produced PA 6 samples from caprolactam using T-RTM. We examined the effects of the manufacturing parameters on morphology on residual monomer content and crystalline proportion. Then we filled the samples with TiO₂ and examined the same parameters. Finally, we tested the effects of crystallinity, residual monomer content and the filler on moisture absorption.

1. Introduction

Nowadays, composites have a significant role in the manufacturing of technical components, due to their low weight (because of their low density) and their excellent mechanical properties. Being recyclable, thermoplastic matrix composites are increasingly used because of their excellent heat resistance, stiffness and high strength. Thermoplastic materials have high viscosity (10-100 Pas) in the melted state, therefore they cannot properly impregnate a continuous reinforcing material. This problem can be solved by caprolactam, which, in the melted state, has a viscosity (3-5 mPas) similar to that of water. Caprolactam can be used to produce polyamide 6 if combined with the appropriate initiator and activator, in a closed mould by ring opening in-situ polymerisation. These polyamides belong to the group of technically significant polymers. They have excellent mechanical properties, but their hydrophilic attribute limits their application. T-RTM (Thermoplastic Resin Transfer Moulding) is a highly efficient automated processing technology for in-situ polymerisation, whereby ring opening polymerization is carried out at low pressure with a sufficiently short cycle time in the shaping mould [1-4].

We produced polyamide 6 samples from caprolactam by T-RTM using TiO₂ as filler. The aim of our study is to analyse the effect of technological parameters, the filler and the environmental conditions on the moisture absorption of the samples. Furthermore, we studied the effect of the morphological structure of the specimens on water uptake.



2. Materials and Methods

2.1. Materials

The polyamide 6 specimens were prepared by anionic ring-opening polymerization from a system of ϵ -caprolactam. The system contained ϵ -caprolactam (AP-Nylon), hexamethylene-1,6-dicarbonyl caprolactam (Brüggolen C20P) as activator and sodium caprolactam as initiator (Brüggolen C10) which was purchased from L. Brüggemann GmbH and Co. KG, Germany. The filler used was titanium dioxide (Titan Dioxide KTR 600, KOLTEX COLOR s.r.o., Czech Republic) which size is 45 μm .

2.2. Sample preparation

The 290 mm \times 510 mm \times 5.5 mm specimens were produced below the melting point of polyamide 6 (130–170 $^{\circ}\text{C}$), by anionic ring opening in-situ polymerisation with the use of the T-RTM (Thermoplastic Resin Transfer Moulding) technology of KraussMaffei Technologies GmbH. The equipment consisted of a DU (Dosing Unit) and a hydraulic press, which is the shaping mould carrier (Figure 1). The DU, whose temperature is 110 $^{\circ}\text{C}$, is suitable for melting the raw materials in an inert nitrogen atmosphere. One DU has two tanks for melting the CL + C10 compound and the CL + C20P + filler separately. In our case, the filler was TiO_2 .

The DU is connected to the forming mould installed on the press with the use of heated pipes, one for CL + C10 and one for the CL + C20P + TiO_2 blend. The pipes are connected to a mixing head, whose temperature is also 110 $^{\circ}\text{C}$. The mould was filled with the melt through them. The components come into contact with each other directly after the mixing head in the cavity. Proper mixing of the components is ensured by the design of the mixing head and the flow rate of the components. Furthermore, there is vacuum in the mould for the best possible filling and the proper temperature ensures polymerisation. After polymerisation, the sample was removed.

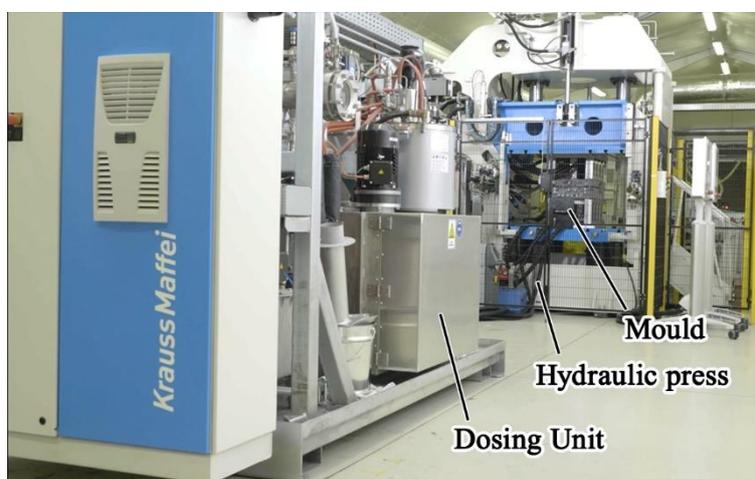


Figure 1. T-RTM machine of KraussMaffei

2.3. Design of experiments

Based on our literature research the most suitable polymerisation time is 3–5 min and the most suitable mould temperature range is 140–190 $^{\circ}\text{C}$. The proposed mixing ratio is 94% from caprolactam, 3% from initiator, and 3% from activator [7-11]. We examined the crystalline ratio and residual monomer content with two different mould temperatures (150 $^{\circ}\text{C}$ and 175 $^{\circ}\text{C}$), and three different residence times (120 s, 180 s and 240 s). Then we prepared TiO_2 filled specimens with the same production parameters and investigated their effect on the crystalline ratio and residual monomer content. The amount of filler added to the system was 0 m/m%, 1 m/m% and 3 m/m%. With more filler, significant sedimentation was observed. We also studied the moisture uptake of samples produced with different mould temperatures and with TiO_2 . Five samples were produced, then crystallinity, residual monomer content

and their effects on moisture absorption were examined. Table 1. and Table 2. show the manufacturing and test parameters of the specimens.

Residence time means the time from the injection of the material into the cavity until take out the finished sample. Mould temperature is the temperature of the tool during production. Filler content is TiO₂ concentration. During production, these parameters determine the morphological structure of the specimens (molecular weight, crystalline structure and proportion, residual monomer content, etc.).

Table 1. Manufacturing parameters

Mould temperature	Residence time		
	120 (s)	180 (s)	240 (s)
150 (°C)	x	x	x
175 (°C)	x	x	x

Table 2. Test parameters

Filler content	Relative humidity	
	50(%)	under water
0 (m/m%)	x	x
1 (m/m%)	x	x
3 (m/m%)	x	x

2.4. Characterization of the samples

The samples were produced with a mould temperature of 150 °C and 175 °C and a residence time of 120 s, 180 s and 240 s and they contain different amounts of TiO₂. Residual monomer content was determined with TGA tests on a TGA Q500 instrument (TA Instruments, New Castle, USA) at temperatures from 50 °C to 350 °C with a heating rate of 10 °C/min. The crystalline proportion of the samples was defined with a TA DSC Q2000 device (TA Instruments, New Castle, USA). We took the measurement in a heat-cool-heat cycle from 25 °C to 250 °C with a heating and cooling rate of 10 °C/min. The first heating gave the information about the production parameters, and the second heating described the properties of the material. The crystalline proportion of the specimens was determined as follows:

$$X = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f \cdot (1 - \phi)}, \quad (1)$$

where ΔH_{cc} is the enthalpy of cold crystallization, ΔH_m is the enthalpy of melting, and ΔH_f is the melting enthalpy of a theoretically fully crystalline polymer ($\Delta H_f = 188$ J/g [12] in the case of PA 6) and ϕ is the mass fraction of the filler.

The water uptake was tested on 40x15x2 mm sized, rectangular samples. They were placed in a desiccator with 50% relative humidity and under water for analysis. Before the tests, we dried the samples in a dryer at 80 °C for 24 hours to remove moisture. During the tests, the weights were measured at predetermined intervals. In the first step, we removed the samples from the desiccator and wiped off the water and vapour on them. Then we measured the mass of the specimens with an Ohaus balance. The mass-specific moisture uptake was determined with Vas-Nagy equation as follows [13]:

$$m(t) = m_{\infty} \cdot \sqrt[3]{1 - e^{-\sqrt{\left(\frac{2t-c}{m_{\infty}}\right)^3}}, \quad (2)$$

where $m_t(t)$ is the mass increase of the sample at the time of water uptake relative to the sample mass before water uptake, m_{∞} is the saturation moisture content of the sample, t is the time of water uptake and c is a constant. The moisture content of the samples was determined as follows [13]:

$$N_{calculate,up} = \frac{m_v(t) - m_{ve}}{m_v(t)} \cdot 100 = \frac{m(t)}{m_v(t)} \cdot 100, \quad (3)$$

where $N_{calculate,up}$ is the measured moisture content of the sample, m_{ve} is the mass of the sample before water absorption, $m_v(t)$ is the mass of the sample measured at the time the water was taken.

3. Results

3.1. Monomer concentration

Residual monomer is the monomer that remains unreacted during polymerisation. It reduces the final conversion and it acts as a plasticizer inside the material, over 4%. It can condense onto the surface of the product, which prevents coating it. In the case of a composite material, it can reduce the interfacial bonding of the matrix and reinforcing material, thereby impairing mechanical properties.

The residual monomer fraction was determined by TGA [14]. Our tests showed that the decomposition temperature of caprolactam is around 200 °C, which is below the melting temperature of PA 6. Figure 2. shows a typical TGA curve of PA 6, where three different temperature ranges can be separated: the first is when the water evaporates from the sample at a temperature of about 80-100 °C, and the second is between 100-250 °C, where the solvents and small molecules (monomers, oligomers) are removed. Finally, the molecular chains begin to break up, and the polymer degrades when heated above the melting temperature.

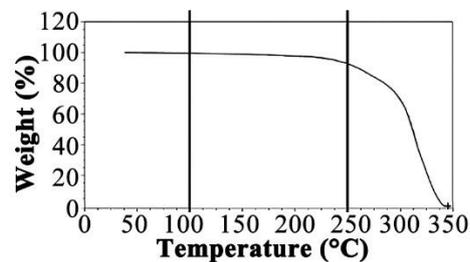


Figure 2. TGA curve of polyamide 6 sample

Conversion is 95-97% at a mould temperature of 150 °C (Figure 3. a)). Monomer ratio decreases when mould temperature increases. This may be the reason why the thermodynamic equilibrium of the monomer and polymer shifts toward the polymer at lower temperatures. A further reason can be that the crystalline phase means a full conversion, hence when crystalline fraction increases, conversion increases also. Residence time does not significantly influence conversion.

We also measured the residual monomer content of the TiO₂ filled samples. The results show that an increase in the amount of TiO₂ (Figure 3. b)) causes the residual monomer content of PA 6 to decrease. Perhaps TiO₂ can stabilize or induce the polymerization process.

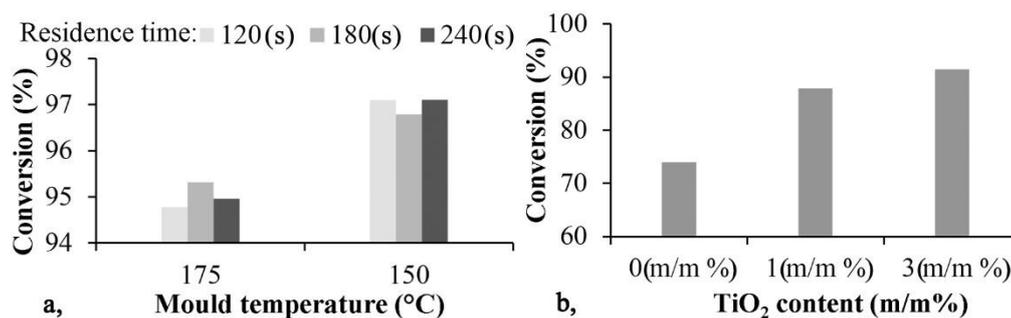


Figure 3. Conversion as a function of mould temperature (a) and TiO₂ content (b)

3.2. Crystalline proportion

We performed DSC tests on the polyamide-6 based specimens to determine the crystalline proportion. Figure 4. shows the crystalline proportion as a function of mould temperature. The specimens prepared with a mould temperature of 150 °C have higher crystallinity than the specimens prepared with a mould temperature of 175 °C. The crystalline proportion is approx. 40–43% in samples produced at the lower mould temperature, and it decreases linearly with increasing mould temperature (at 175 °C it is 20%). Residence time does not significantly influence crystalline proportion.

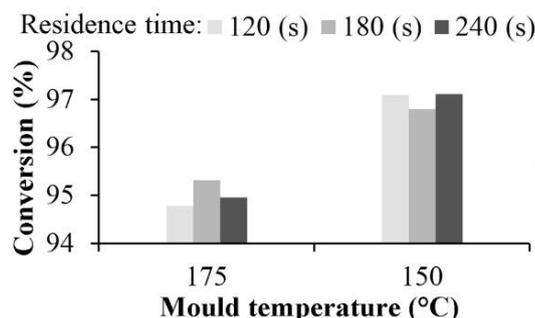


Figure 4. Crystallinity as a function of mould temperature

Figure 5. shows the results of the DSC test. The tests were performed on PA 6 specimens filled with 0 m/m%, 1 m/m% and 3 m/m% TiO₂. Samples of around 5 mg were used for the tests.

The curves show the effect of TiO₂ as a nucleating agent in PA 6 specimens produced by in-situ polymerisation and PA 6 manufactured by a melt process (like injection moulding, extrusion or compression moulding). In in-situ polymerisation, the TiO₂ slightly reduces crystallinity, while it increases the crystalline proportion in the specimen produced from melt. In the first heating stage, increasing TiO₂ content widens the crystallization range and the peaks shift to lower temperatures. The first cooling section shows the nucleation effect of TiO₂ during production from melt. In this case, increasing amounts of TiO₂ cause narrower crystallization ranges and the peaks shift to higher temperatures. Consequently, TiO₂ is an effective nucleating agent for polyamide 6.

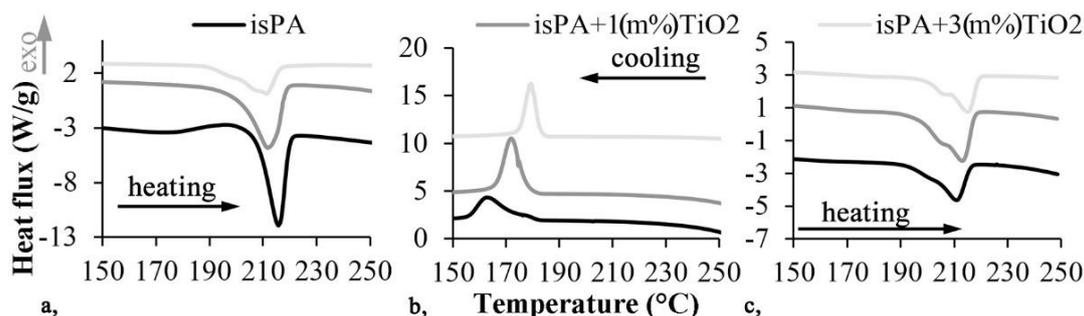


Figure 5. Heating curves for the DSC test: First heating (a), First cooling (b), Second heating (c)

The results of evaluation are shown in Figure 6. which clearly shows that increasing the amount of TiO₂ in the specimens produced by in-situ polymerisation reduced the crystalline proportion. In contrast, the crystalline proportion is significantly increased when the amount of TiO₂ is increased in specimens produced from melt. This may be important in the recycling of in-situ polymerised products, because the fillers in the surface coating can increase the crystalline content of the recycled material, thereby reducing moisture absorption.

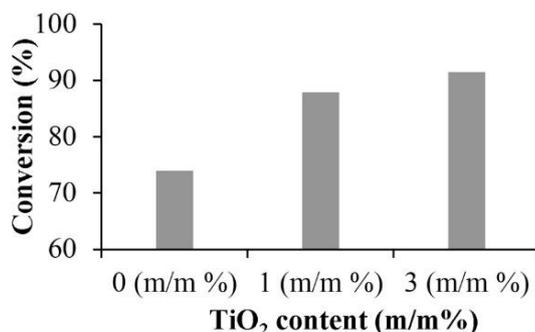


Figure 6. Crystallinity as a function of TiO₂ content

3.3. Moisture absorption

Due to hydrophilic properties of PA 6, it can absorb water, which also has a major influence on its mechanical properties. Moisture has a softening effect, thereby reducing elastic modulus, strength and hardness. It causes a significant increase in the size of specimens due to the swelling of the polymer. This must be taken into account with strict tolerance for the reproducibility of the product [15].

Figure 7. a) shows as a function of time the measured and calculated moisture content of specimens produced with a mould temperature of 150 °C, and Figure 7. b) shows the same for 175 °C. The DSC tests show that the specimens produced with the higher mould temperature have a lower crystalline ratio; at 175 °C crystalline ratio is 21.2% and at 150 °C it is 41.7%. Samples produced with a mould temperature of 175 °C absorbed more water in all test environments than samples produced with 150 °C. This is due to their lower crystalline proportion, because only the amorphous phase is able to absorb water in semicrystalline polymers [15]. We proved that the moisture uptake formula can describe the whole process well; the measured and calculated results correlate well.

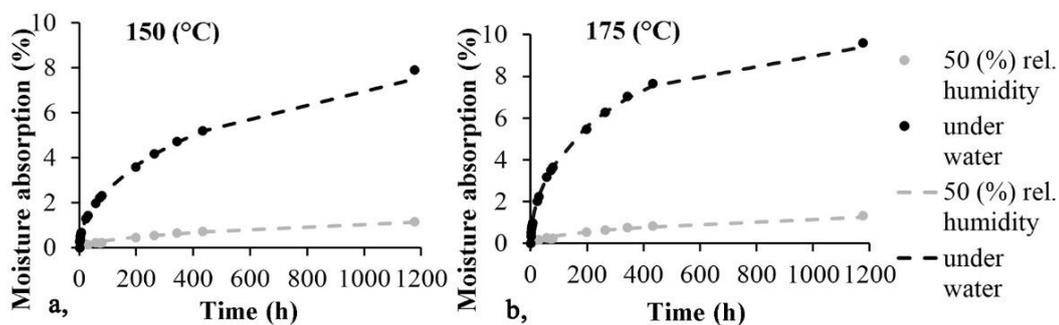


Figure 7. Moisture content as a function of residence time on mould temperature of 150 °C (a) and 175 °C (b)

The specimens filled with different amounts of TiO₂ were produced with a mould temperature of 150 °C and a residence time of 240 s. At 50% humidity, the measured and calculated moisture content of the specimens as a function of time is shown in Figure 8. a). The DSC tests show that increasing the amount of TiO₂ from 1 m/m% to 3 m/m% reduces the crystalline proportion from 40% to 37.1% in in-situ polymerisation specimens. Increasing TiO₂ content decreases water uptake because only the PA can absorb moisture; the TiO₂ does not. In the case of 3 m/m% TiO₂, the decrease is 2.4%, while it is around 2.9% in unfilled specimens. Figure 8. b) shows the measured and calculated moisture content of the specimens under water, as a function of time. During the construction of the model, the values marked with the red ellipse were ignored. This can be explained by the less than 100% conversion rate. The specimens have a residual monomer content of 4-5%, which is dissolved by the water, therefore the weight of the specimen is reduced. Contrary to expectations, the 0 m/m% TiO₂ specimens have a lower water content, due to its higher monomer content and consequently the monomer is dissolved by the water. The measured and calculated results are in good agreement, so the proposed formula can also be used to evaluate TiO₂ filled specimens.

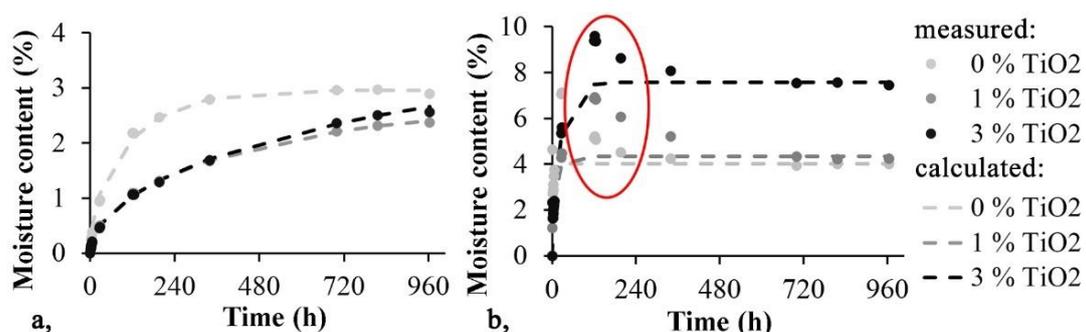


Figure 8. Moisture content as a function of residence time at 50% humidity (a) and under water (b)

Table 3. shows the result of the moisture absorption.

Table 3. Result of the moisture absorption

	Crystallinity	Moisture absorption		
		50 % rel. hum.	under water	
Mould temperature	175 °C	21.2 %	1.3 %	9.6 %
	150 °C	41.7 %	1.15 %	7.9 %
TiO₂ content	0 m/m %	40 %	2.9 %	4.01%
	1 m/m %	37.3 %	2.37 %	4.24 %
	3 m/m %	37.1 %	2.56 %	7.45 %

4. Conclusions

We produced polyamide 6 specimens from caprolactam by in-situ polymerisation, using T-RTM. Mould temperature and residence time was varied and TiO₂ was used as filler. We studied the effects of mould temperature, residence time and TiO₂ concentration on crystalline ratio, residual monomer content and moisture absorption, and also measured the effect of the crystallinity and residual monomer content of the specimen on moisture absorption.

We found that crystalline proportion decreased (by about 3%) with increasing amount of TiO₂ in the specimens. TiO₂ inhibits the formation of crystals. In addition, PA 6 produced by anionic ring-opening polymerisation has a very high (37-40%) crystalline content. Crystalline proportion significantly increased when the amount of TiO₂ was increased in the samples produced from melt. In this case, the TiO₂ behaves as a good nucleating agent. This may be important in the recycling of in-situ polymerised samples, because the fillers in surface coating can increase the crystalline proportion of the recycled material, thereby improving its mechanical properties and reducing its water uptake. We examined the residual monomer content of the samples. The result was that the monomer content of polyamide 6 decreased with increasing TiO₂ content, and the curves shifted upwards.

Finally, we tested the water absorption of the samples produced with mould temperatures of 150 °C and 175 °C. These samples had different crystalline proportions; the samples produced at 150 °C have 41.7% crystallinity, while the samples produced at 175 °C have 21.2% crystallinity. Samples with a higher crystalline proportion absorbed less moisture. Furthermore, we proved that the TiO₂ reduces the water uptake of PA 6 at 50% relative humidity, but we found the opposite tendency under water.

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