

INFLUENCE of WATER during MANUFACTURING of APA6 in the THERMOPLASTIC RTM PROCESS

Rainer Wendel^a, Bernd Thoma^a and Frank Henning^{a,b}

a Department of Polymer Engineering, Fraunhofer Institute for Chemical Technology (ICT), Joseph-von-Fraunhofer Straße 7, 76327 Pfinztal, Germany

b Institute for Vehicle Systems Technology, Karlsruhe Institute of Technology (KIT), Kaiserstraße 12, 76131 Karlsruhe, Germany

Abstract. The thermoplastic resin transfer molding (T-RTM) process has the potential for high-volume production of high performance fiber-reinforced components in the automotive industry. The fast anionic polymerization of APA6 and the development of robust injection equipment lead to short cycle times. The sensitivity against water of the reactive APA6 is well known. All resin components from the manufacturer are dried to achieve water content below 200 ppm. In T-RTM high-performance composite manufacturing fibers, binder systems or core materials are needed. During the manufacturing (preforming, handling, infiltration) of these materials it is necessary to ensure that the total amount of water is small enough to achieve good polymerization. Previous studies established the influence of water for non-activated polymerization. However, there is no knowledge about the influence of water during T-RTM manufacturing using fast-reacting activated polymerization. In this paper, different concentrations of catalyst are investigated to analyze the influence of water in the T-RTM process during curing of the resin. Residual monomer content and viscosity number was measured to analyze the conversion of manufactured plates. To characterize the impact on the mechanical properties, tensile tests were performed. The results show the possibility to monitor the anionic polymerization during the manufacturing by observing the trend of the cavity pressures. In addition, the influence of water on the conversion and the resulting mechanical properties can be compensated by the concentration of the catalyst.

Keywords: thermoplastic resin transfer molding (T-RTM), cast polyamide 6 (cast PA6), anionic polyamide 6 (APA6), anionic polymerization, moisture, ϵ -caprolactam, thermoplastics

PACS: 81.05.Lg

INTRODUCTION

Plastics are increasingly prevalent in lightweight applications. The advantages they offer over thermosets include their good impact properties, toughness, the possibility of welding and their reusability with secondary manufacturing processes [1,2,3]. The high viscosity of plastics prevents the infiltration of continuous fibrous reinforcements. The manufacturing of reactive plastics provides the advantage of fast infiltration of fabrics with high fiber contents due to the very low viscosity of the monomer melt. The anionic polymerization of ϵ -Caprolactam to APA 6 has been investigated extensively due to the good chemical conversion and the fast polymerization. The use of APA6 in the resin transfer molding process offers a new possibility to manufacture continuous-fiber-reinforced composites with complex geometries.

During the last few years extensive research and development was carried out on the so-called thermoplastic resin transfer molding process. Some demonstrators were also developed for structural parts in automotive applications, such as a b-pillar and roof frame [4,5]. Abisset-Chavanne et al. developed a simulation model for reactive T-RTM processes to predict the mold filling. In this context they considered the thermo-chemico-mechanical couplings. They showed that the crucial parameter is the evolution of resin viscosity with the polymerization degree for the filling [6]. Schell et al. studied process variants like compression RTM for low viscosity thermoplastics to avoid fiber washing and to reduce cycle time [7]. Flame retardant additives were developed for the manufacturing of APA6 in T-RTM by Höhne et al [8]. Verrey and co-workers conducted a cost study of automotive body-in-white structures for thermoplastic and thermoset RTM [9]. Ehleben et al. showed the potential to use T-RTM for the new, large-scale production of an automotive application like the b-pillar. The good drapability of the dry preforms is an advantage compared with forming technologies, which are limited by geometrical issues [10].

However, there was skepticism about manufacturing in product lines, due to the sensitive influence of water during the anionic polymerization. Reimschüssel et al. and Bernat et al. have analyzed the influence of water on non-activated polymerization on a lab scale [11,12]. Even the resin suppliers recommend the manufacturing of reactive monomer under dry and oxygen-free conditions, because the oxygen in water and the air hinders the reaction. A

robust and reproducible process with well-known constraints is essential for production. All resin components from the manufacturers are dried to achieve water contents of less than 200 ppm. In T-RTM high-performance composite manufacturing, fibers [13, 14, 15, 16], binder systems or core materials are therefore needed. During T-RTM manufacturing it is important to ensure that the total amount of water in these materials in each process step (preforming, handling, infiltration) is small enough to achieve good polymerization. In this study the influence of water on fast, activated polymerization is investigated in the T-RTM manufacturing process.

For manufacturing using the T-RTM processes it is important to understand the influence of water on the anionic polymerization and to know threshold values for the manufacturing. In this study the influence of water for different concentrations of activator and catalyst is investigated during the T-RTM manufacturing process. The impact on the mechanical properties is also described.

EXPERIMENTAL PROCEDURES

For the manufacturing of APA6 the monomer ϵ -Caprolactam, the activator Brüggolen C20 and the catalyst Brüggolen C10 from Brüggemann Chemical were used. The ratio of 1:2 of activator and catalyst was kept constant due to the bi-functionality of the activator. The following concentrations of activator and catalyst were used:

TABLE 1. Formulations with different concentration of activator and catalyst

Formulation	Concentration Activator C20	Concentration Catalyst C10
F1	1%	2%
F2	1,5%	3%
F3	2%	4%
F4	2,5%	5%

Unreinforced APA6 plates (900x550x2mm³) are manufactured via T-RTM processing. The manufacturing equipment consists of a low-pressure T-RTM injection machine from ATP, a press Type 630 DYL from Dieffenbacher and a plate mold. The resin components ϵ -Caprolactam, activator and catalyst were stored in the vessels of the injection machine at 98°C. Defined amounts of water are added in the vessels. After 5 minutes mixing the next trials are performed.

For the tensile test measurements, an inspect table 50kN tester (Hegewald & Peschke) with a 50 kN-measuring box and a test speed of 1 mm/min were used. The tests were carried out according to DIN EN ISO 527-1 standard. The samples for the tensile test were dried for 72 h at 80 °C to achieve constant weight. The residual monomer content of the samples was extracted with water and measured with a HPLC laboratory device Agilent 1100 Series. The viscosity number was investigated with an ubbelohde viscometer according to DIN 51562. The measurements were carried out at 20°C. The solvent of the polymer was 95% sulfuric acid.

RESULTS AND DISCUSSION

The anionic polymerization is monitored during the T-RTM manufacturing process by measuring the cavity pressures during the injection and curing of the reactive components in the mold. First the cavity pressure of different formulations is tested with 0% water (Figure 1) to understand the influence of the concentration of activator and catalyst on the cavity pressure.

The manufacturing T-RTM process can be divided into 3 phases: Vacuum application, injection and curing. At the beginning of the T-RTM process, a vacuum is applied for 30 seconds after closing the mold. The injection is then started, and the cavity pressures increase as the cavity is filled. After the injection is completed the injection point in the mold is closed and the clamping force of the press is increased. The cavity pressures increase up to their maximum. Subsequently the cavity pressures decrease and reach a plateau at about 50 bar. The shape of this plateau depends on the amount of activator and catalyst. Afterwards, the pressures drop to 0 bar. The increase of activator and catalyst leads to a drop in the cavity pressure after 50 bar. The time until the pressures drop to 0 bar is much shorter.

The cavity pressures show a regressive trend after applying the dwell pressure. This decrease is caused by shrinkage which takes place due to polymerization and crystallization during the anionic polymerization [17]. A probable reason for the fast decrease after the plateau is that the material becomes solid and loses contact with the pressure sensor. The higher the concentrations of activator and catalyst, the faster the conversion of the monomers [18, 2].

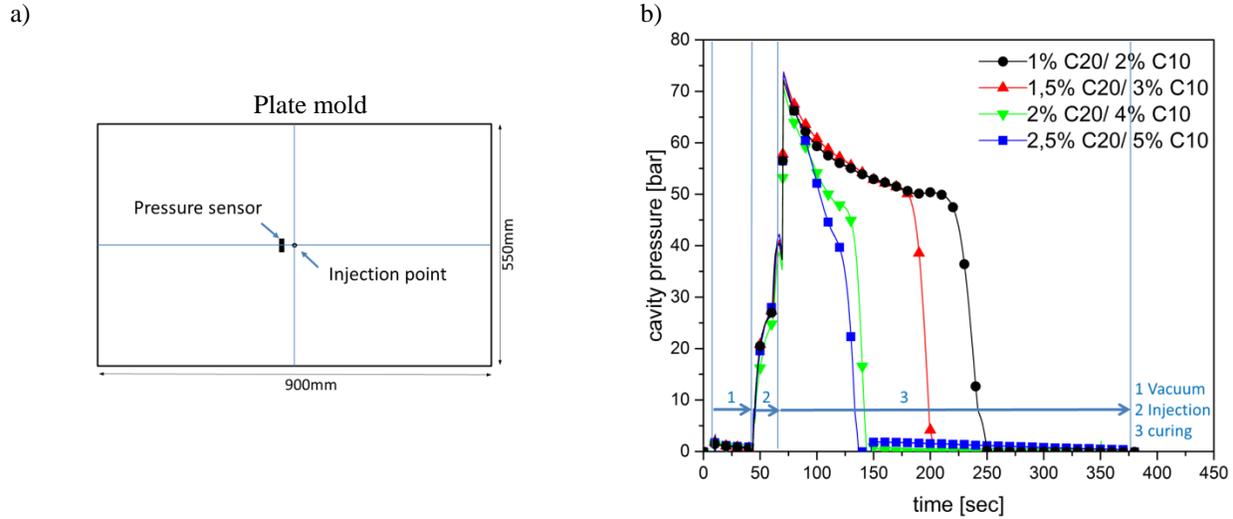


FIGURE 1. Position pressure sensor (a) and cavity pressures of different formulations with 0% water (b)

For the characterization of the anionic polymerization during the T-RTM manufacturing process, the water content in the reactive melt was increased gradually by 0.02%. For all formulations it can be seen that the addition of water slows the regressive decrease of the cavity pressures and strengthens the plateau before the pressure falls away sharply. With increasing water content it takes longer for the pressures to drop to a minimum. This decrease did not take place until the mold opened. The reaction was not finished. The part could therefore not be demolded. This could be seen for all formulations. 0.02% water added to F1 is enough to prevent curing of the melt within 300 seconds curing time (Figure 2). Another trials were made with F1 and 0,02% water. The curing time was changed to 500 seconds. The graph shows a decrease of the pressure before the mould opens. The plates were cured after 500 seconds curing time.

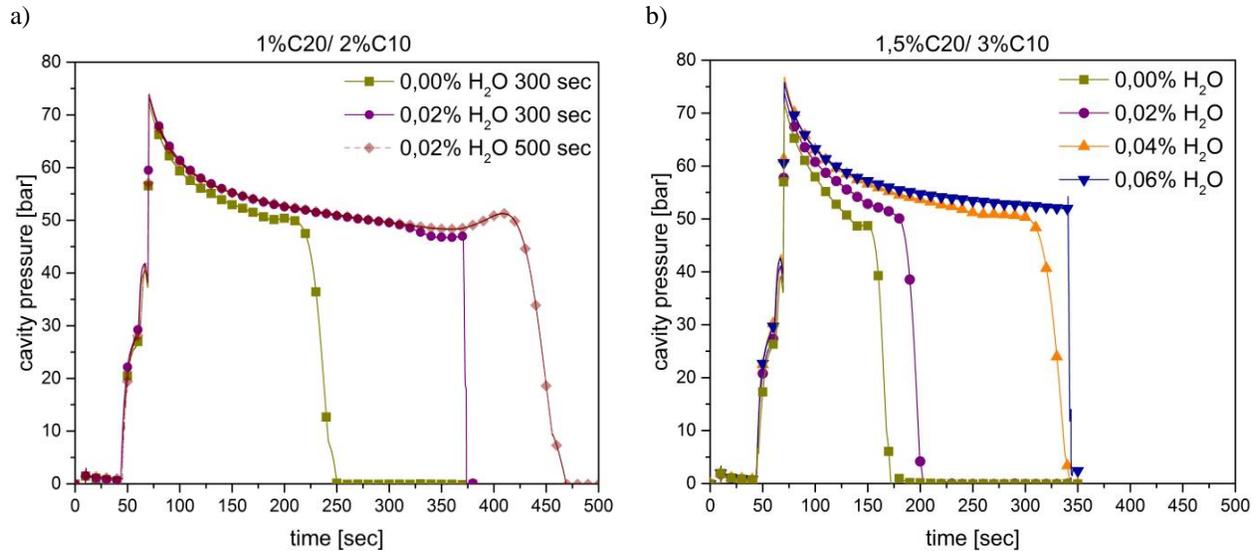


FIGURE 2: Cavity pressures during curing of formulation 1 (a) and formulation 2 (b)

With the extension of the curing time, and consequently the later opening of the mold, the curing takes place. At 1.5% activator and 3% catalyst the demolding with 0.04% water is possible. The pressure trends show a rapid decrease of the pressure shortly before opening the mold. At a water content of 0.06% there is no decrease after achieving the plateau. No polymerization occurred until the mold opened.

The manufacturing of solid plates with F3 is possible for water contents up to 0.06% (Figure 3a). A further increase of water up to 0.08% prevents the polymerization for a curing time of 300 seconds until the mold opens. The formulation with 2.5% activator and 5% catalyst shows similar trends (Figure 3b). The manufacturing of cured

plates is possible for water contents of up to 0.08%. At 0.1% water, the area in the cavity at the pressure sensor is not cured.

The comparison of the cavity pressures of the different formulations of activator and catalyst reveals a significant difference. The lower the activator/catalyst concentration, the less water can be added before the anionic polymerization of the reactive melt stops. The presence of water initiates a side reaction [19]. The catalyst is consumed. There are fewer anions available for the reaction. By extending the closing time of the press the T-RTM process can be adjusted to allow the melt to cure and to demold the part. Time spent cleaning non-reacted material from the mold can be saved. At small amounts of activator and catalyst the cavity pressure needs more time to drop. The shrinkage of the material during reaction is slower due to the lower conversion rate of the reaction.

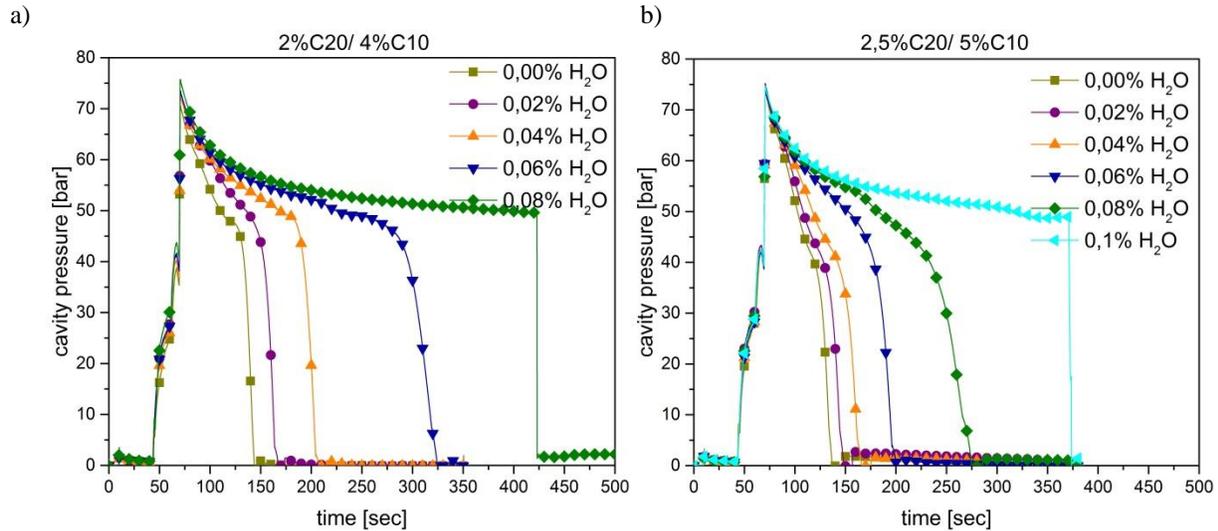


FIGURE 3: Cavity pressures during curing of formulation 3 (a) and formulation 4 (b)

The mechanical properties were measured in tensile tests. The mechanical testing was only possible with polymerized samples which could be demolded as solid plates after the curing time of 300 seconds.

In Figure 4 the tensile properties of the manufactured plates are shown with different water contents during curing. The reduction of the activator and catalyst increases the tensile stiffness of the samples with 0% water content. The influence of the concentration of activator/catalyst on the tensile strength is negligible. The addition of water influences the stiffness and strength of the cured material. At small concentrations of activator and catalyst the reaction is extremely sensitive. Small amounts of water (0.02%) lead to a significant decrease in stiffness and strength. The decrease of stiffness and strength at higher concentrations of activator and catalyst therefore occurs only at higher concentrations of water.

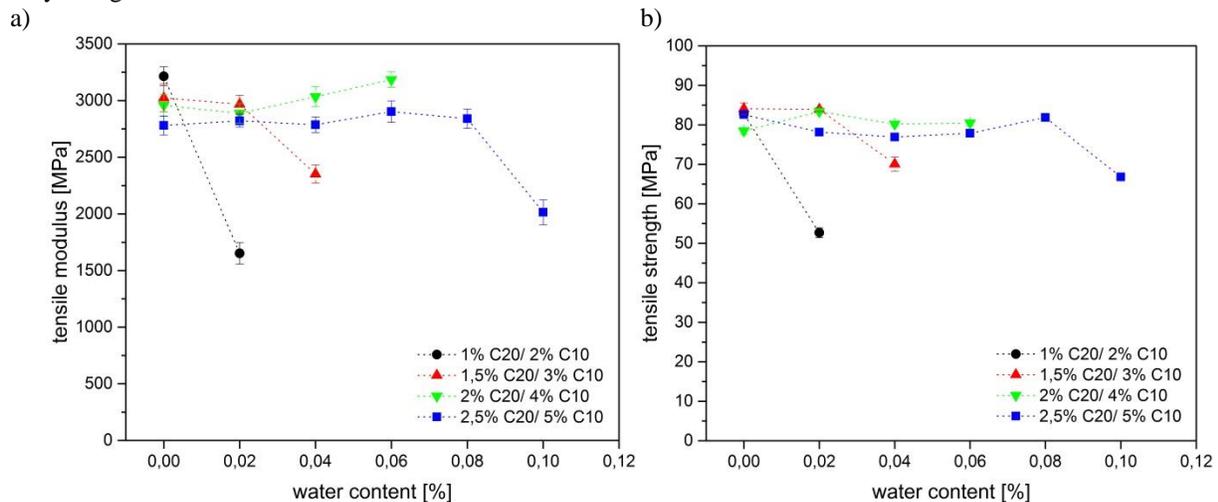


FIGURE 4: Influence of water on tensile modulus (a) and strength (b)

Zhang et al. investigated methods to measure the conversion rate [20]. The residual monomer content (RC) and the viscosity number (VZ) is used in this study as an indicator for the conversion of the anionic polymerization. The RC indicates the monomer content which is not converted during the reaction. The VZ is directly related to the average molecular weight, and can be used as one indicator for the rate of the polymerization [21].

In Figure 5 the RC of the formulations are shown. A RC of 1% builds the threshold value for good polymerization. F1 with only 1% activator and 2% catalyst is extremely sensitive to water. The RC of F1 increases from 0.6% up to 12 % on the addition of 0.02% water. For F2, 3 and 4, with higher concentrations of activator and catalyst this increase of RC fails to appear at water contents of 0.02%. F2 shows a higher RC of 1.8% with 0.04% water. The increase in RC at F3 starts at 0.06%. Due to the buffering of F4 the increase occurs at 0.1% water.

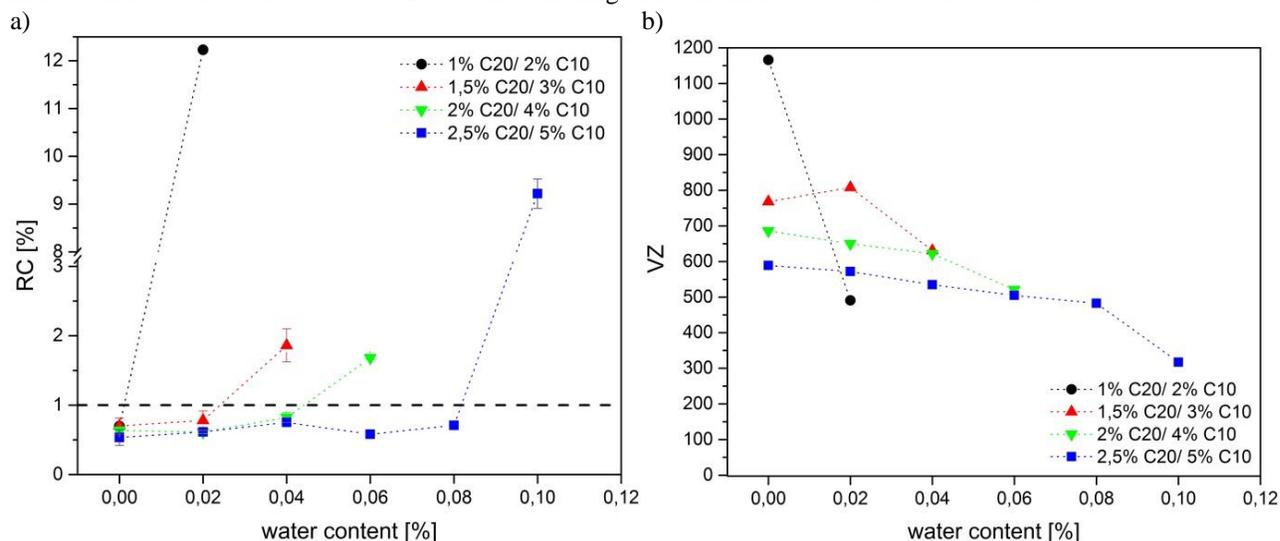


FIGURE 5: Influence of water on residual monomer content (a) and viscosity number (b)

The VZ offers valuable clues about the conversion of the anionic polymerization. The results with 0% water show a significant difference between the individual formulations. As expected, the concentration of the activator and catalyst influences the VZ. At low concentrations of activator and catalyst the VZ is much higher than at higher concentrations of activator and catalyst [Figure 5]. The graph only shows the average because the standard deviation of the three measurements is negligible (about 1 %). The VZ decreases when water is added. This effect can be seen for every formulation. The decrease of VZ when water is added depends on the formulation. Low concentrations are more sensitive to water. At low concentrations of activator and catalyst the decrease on adding water occurs much faster than at higher concentrations.

The influence of activator and catalyst on the mechanical properties can be seen in the tensile tests with 0% water. F1 with the lowest content of activator and catalyst shows the best properties and the highest molecular weight.

The increase in the amount of residual monomer at low concentrations of activator and catalyst starts at lower amounts of water. The water molecules deactivate the reactive groups. As more reactive groups are deactivated, the RC increases. With increased concentration of the activator and catalyst the reactive system is tougher against water or humidity because more anions are available for the reaction. However, the influence of water or humidity is still a major determining factor which cannot be neglected. It is important to ensure that the amount of water in the system (machine, resin components, fibers, cores) does not exceed the threshold values to ensure reproducible manufacturing. The VZ of anionically manufactured PA6 is higher than that of hydrolytically manufactured PA6. Measurements of hydrolytically manufactured PA6 (Ultramid B3K) showed a VZ of 150. The higher VZ of anionically manufactured samples can be attributed to the higher molecular weight. The molecular chains break during cleaning of the polycondensated materials due to the high temperatures, solvents and high shear forces. The molecular weight is reduced to lower the melt viscosity to enable manufacturing [22].

The results of RC are well in line with the results of VZ. A quality fall-off takes place at the same concentration of water. F1 shows this quality fall-off at 0.02%, F2 at 0.04%, F3 at 0.06% and F4 at 0.1%.

CONCLUSION

In this study, fast activated anionic polymerization was investigated for the T-RTM manufacturing process. The influence of water on the curing time was demonstrated. The presence of water does not stop the polymerization, but it slows the reaction by deactivating the reactive components.

The results show the possibility of monitoring the rate of anionic polymerization during manufacturing by observing the trend of the cavity pressures. The absorption and the delivery of water in semi-finished products like preforms will be carried out in future studies. Necessary pretreatments will be deviated with the results of these studies.

ACKNOWLEDGEMENTS

We thank Ronny Hanich (Fraunhofer ICT) for performing many of the measurements presented, and Matthias Stricker (Fraunhofer ICT) for the tests with the ubbelohde viscosimeter, Uwe Podwojewski (Fraunhofer ICT) for the tensile tests and Anja Kaiser (Fraunhofer ICT) for the residual monomer measurements. We also thank Cahit Arik (Fraunhofer ICT) for performing the T-RTM process, and Brüggemann Chemical for providing the materials.

REFERENCES

- 1 D. Stavrov; H.E.N. Bersee, "Resistance welding of thermoplastic composites-an overview", *Compos. A: Appl. Sci. Manuf.* 2005, 36, 39.
- 2 P. Hodge, "Cyclodepolymerization as a method for the synthesis of macrocyclic oligomers", *Reactive & Functional Polymers* 80 (2014) 21-32
- 3 B. R. Formisano; C. Bonten; "Recycling von Gusspolyamid-Abfällen", *WAK Journal of Plastics Technology* 2016
- 4 M. Bitterlich; M. Ehleben; A. Wollny; P. Desbois; J. Renkl; S. Schmidhuber, "Tailored to Reactive Polyamide 6", Carl Hanser Verlag, Munich, *Kunststoffe International* 3/2014
- 5 S. Schmidhuber; E. Fries; P. Zimmermann, "It couldn't be more hybrid", Carl Hanser Verlag, Munich, *Kunststoffe international* 1-2/2017
- 6 E. Abisset-Chavanne; F. Chinesta, "Toward an optimisation of the reactive resin transfer molding process: thermo-chemico-mechanical coupled simulations", *Int J Mater Forming*. DOI: 10.1007/s12289-013-1124-0.
- 7 J.S.U. Schell; H. Aimé; S. Comas-Cardona; Ch. Binetruy; A. Lemasçon; M.F. Lacrampe ; M. Deléglise-Lagardère, *ITHEC 2014, MESSE BREMEN*
- 8 C.-C. Höhne; R. Wendel; B. Kabisch; T. Anders; F. Henning; E. Kroke; "Hexaphenoxycyclotriphosphazene as FR for CFR anionic PA6 via T-RTM: a study of mechanical and thermal properties" *Fire Mater*, 2016
- 9 J. Verrey; M.D. Wakeman; V. Michaud; J.-A.E. Manson, "Manufacturing cost comparison of thermoplastic and thermoset RTM for an automotive floor pan", *Composites: Part A* 37 (2006) 9–22
- 10 M. Ehleben; M. Bitterlich; O. Täger, "New industrial-scale production processes for thermoplastic fibre reinforced polymer parts", *VDI Conference* 2015
- 11 H. K. Reimschuessel, "Nylon 6 Chemistry and Mechanisms" *J. POLYMER SCI.: Macromolecular Reviews*, Vol. 12,65-139 (1977) by John.Wiley & Sons, Inc
- 12 P. Bernat; O. Hladká; M. Fišmanová; J. Roda; J. Brožek; "Polymerization of lactams. 98: Influence of water on the non-activated polymerization of ϵ -caprolactam" *European Polymer Journal* 44 (2008) 32–41
- 13 R. Hoto; J. Andres; B. Cabillic; L. Gascon; J.A. Garcia, "Optimization of mechanical properties of basalt woven/APA-6 composite parts by means of velocity control". 18th international conference on composite materials
- 14 S. Pillay; U. K. Vaidya; G. M. Janowski, "Liquid Molding of Carbon Fabric-reinforced Nylon Matrix Composite Laminates *Journal of Thermoplastic Composite Materials*", Vol. 18 (2005) 509
- 15 A. Alfonso; R. Hoto; J. Andrés; J.A. Garcia, "Industrial viability of APA-6 matrix-based basalt fiber reinforced composites" 18th international conference on composite materials
- 16 Chun Yan, Hongzhou Li, Xiaoqing Zhang, Yingdan Zhu, Xinyu Fan, Liping, "Preparation and properties of continuous glass fiber reinforced anionic polyamide-6 thermoplastic composite"s *Materials and Design* 46 (2013) 688-695
- 17 P.P. Parlevliet; H.E.N. Bersee, "Measurement of polymerization shrinkage of matrices for liquid moulding"
- 18 N. Barhoumi; A. Maazouz; M. Jaziri; R. Abdelhedi, Polyamide from lactams by reactive rotational molding via anionic ring-opening polymerization *Polymer Letters* Vol.7, No.1 (2013) 76–87
- 19 K. Ueda; K. Yamada; M. Nakai; T. Matsuda; M. Hosoda; K. Tai, "Synthesis of high molecular weight nylon 6 by anionic polymerization of ϵ -caprolactam" *Polym J* 1996;28:446–51
- 20 C.-L. Zhang; L.-F. Feng; G.-H. Hu, "Anionic polymerization of lactams: A comparative study on various methods of measuring the conversion of ϵ -caprolactam to polyamide 6" *Journal of Applied Polymer Science*, Vol. 101, 1972–1981 (2006) Wiley Periodicals, Inc.
- 21 K. Ueda; M. Nakai; K. Hattori; K. Yamada; K. Tai, *Kobunshi Ronbunshu* 1997, 56, 401

-
- 22 K. van Rijswijk; H.E.N. Bersee, "Reactive processing of textile fiber-reinforced thermoplastic composites – An overview"
Composites: Part A 38 (2007) 666–681