Direct Compounding of Polyamide 6

From Monomer to Compound in One Single Step

Following anionic polymerization of polyamide 6, a high amount of residual monomers is usually left in the extruder that is why this process has not found its way into industrial application yet. Multi-stage vacuum degassing can reduce the content of residual monomers in the process. If adding a filler, this enables direct compounding of PA6 compounds.

Thanks to its high reaction rate, polyamide 6 (PA6) can be synthesized from ε-caprolactam by anionic polymerization, if applying an activator and a catalyst. Similar to hydrolytic polymerization in the large reactors of chemical industry, a temperature-related share of approx. 10 wt. % of residual monomers remains in the PA6. To achieve good product quality, the residual monomer content must be reduced to < 1 wt. % prior to further processing [1].

Thanks to the twin-screw extruder's modular design, the processor can link the step of continuous polymerization reaction to additional process stages, without the need to re-melt material. This is how a single process step can comprise polymerization, vacuum degassing of the melt in order to reduce residual monomer content, as well as filler addition, without requiring an additional step of residual monomer removal. These compounds obtained from "initial heat" can be processed directly. Via the activator content, the molecular weight of the PA6 material can be set precisely. A twin-screw extruder is able to process high molecular weights, in particular, which cannot easily be performed in a large chemical reactor [1].

The course of anionic polymerization of PA6 has been described in detail before [2, 3]. The chains tend to grow starting from the activator molecules, which is why molecular weight can be set via activator content. As activator content is reduced, molecular weight rises. By adding, e.g., water, the catalyst can be deactivated in well-aimed way, after the expiry of polymerization reaction.

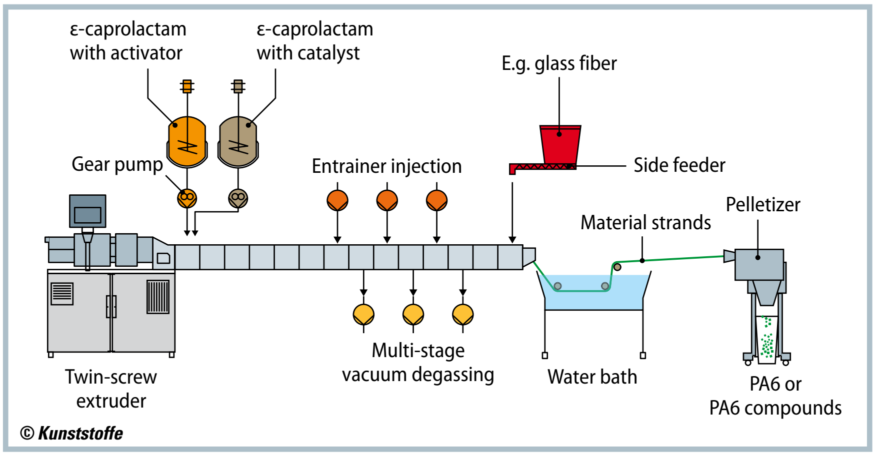

Fig. 1. Machine design for the reactive extrusion of polyamide 6 with integrated multi-stage residual monomer degassing and addition of filler

Extrusion Includes Removal of Residual Monomers as well as Addition of Filler

The low-viscous reaction system for the anionic polymerization of PA6 is provided by Brüggemann Chemicals KG in Heilbronn, Germany. From two heated stirred tanks, the system is fed into the co-rotating twin-screw extruder via gear pumps (**Fig. 1**). The extruder is a ZSK26Mc of Coperion GmbH in Stuttgart, Germany, with 26 mm screw diameter and 56 D length. The reaction system is mixed in the extruder, where the polymerization reaction is thermally initiated. After reaction is completed, the highly viscous PA6 melt is conveyed from the reaction zone to the degassing zone. Up to three degassing zones of the same structure can be implemented in the process. At the beginning of each degassing zone, water is injected into the melt at high pressure. The water deactivates the active catalyst after polymerization is completed. At the same time, it acts as entrainer to improve degassing performance. In case the catalyst is not deactivated, residual monomers may reconstitute during and after degassing. Following the third degassing zone, fillers can be incorporated. The melt then passes a die head forming two strands. These strands are cooled in a water bath, and pelletized. It will be interesting to consider the molecular weight of the PA6 as to its effect on the residual monomer degassing process. For this purpose, this process will be regarded in the following for PA6 with two different activator contents (0.5 and 2 wt. %).

Reducing the Residual Monomer Content

The more degassing zones there are, the lower the content of residual monomers in the PA6. This is the case with both activator contents (**Fig. 2**). With 10 kg/h melt throughput, a low content of residual monomers, i.e., 1.4 wt. %, was achieved for the PA6 with 0.5 wt. % activator content. Low activator contents means the PA6 material synthesized has higher molecular weight, and, thus, higher melt viscosity. Degassing can therefore be expected to be poorer than with the PA6 including 2 wt. % of the activator. Melt temperature rises up to 370 °C with both activator contents, as the number of degassing zones is increased. »

Practical Benefits

Reactive extrusion of PA6 is linked to multi-stage degassing of residual monomers and addition of fillers. This enables the processor to produce compounds out of the monomer from “initial heat”, and, along with this, to save energy and costs. However, specific material properties can be generated in a well-aimed way by adding fillers affecting the polymerization process. It may also be possible to produce PA6 semi-finished products, e.g., films, by direct extrusion. This will further enhance the potential of reactive extrusion for PA6 materials.

The Authors

Prof. Dr.-Ing. Christian Hopmann holds the chair of plastics processing and is head of the Institute of Plastics Processing (IKV) at RWTH Aachen University, Aachen, Germany.

Dipl.-Ing. Eike Klünker has been part of the IKV scientific staff between 2010 and 2014, working in the areas of reactive extrusion and compounding.

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Service

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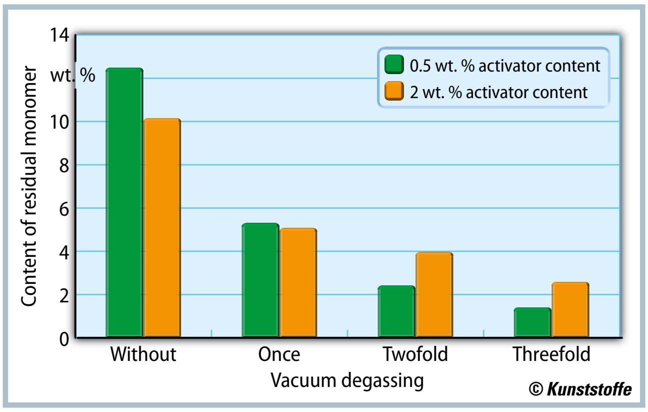

Fig. 2. Contents of residual monomers related to the number of degassing zones and activator content

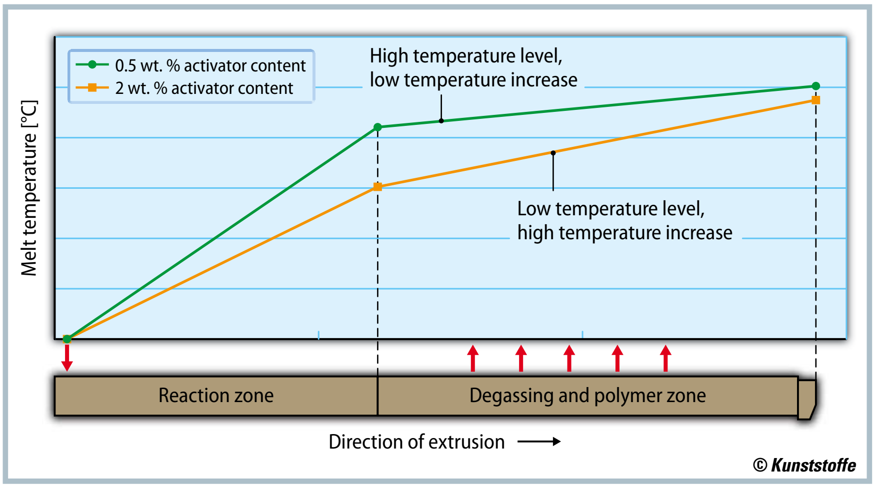

Fig. 3. Schematic presentation of the melt temperature over the course of the process in case of multi-stage residual monomer degassing for PA6 with different contents of activator

Even without vacuum degassing, the PA6 with 0.5 wt.% activator content features a higher temperature level: Its melt temperature is approx. 310 °C, while the melt temperature of a PA6 with 2 wt.% activator content is approx. 250 °C.

The energy dissipated in the melt as a result of shearing behaves proportional to shear rate and melt viscosity. A higher share of shear energy can be dissipated with the PA6 of 0.5 wt.% activator content, due to its higher molecular weight. Therefore, as compared to the PA6 of 2 wt.% activator content, for this variant, melt temperature is already higher following processing in the reaction zone. As the number of degassing zones is increased, a higher amount of residual monomers is removed from the melt, acting like a low-molecular lubricant. Removing residual monomers steps up melt viscosity. This leads to an additional amount of shear energy being dissipated, which increases melt temperature. Based on these facts, one may assume melt temperature over the course of the process as a function of the activator content (**Fig. 3**). The figure clearly shows the higher temperature level for the case of the PA6 with 0.5 wt.% activator content, acting on the melt over the entire course of the process. The PA6 with a 2 wt.% activator content does not achieve a comparable temperature level before reaching the extruder outlet. A high melt temperature has a favorable effect on degassing performance. This can explain the degassing result for the PA6 with a 0.5 wt.% activator content, which at first glance seems contradictory.

Melt throughput also has a critical effect on degassing performance. As melt throughput rises, the melt’s average residence time in the degassing zones decreases, while the screw’s filling degree is increased. These effects deteriorate degassing. If reducing melt throughput to 5 kg/h, a minimum content of residual monomers can be achieved of 0.9 wt.% for the PA6 with a 0.5 wt.% of activator content, in the case of three-stage residual monomer degassing (**Fig. 4**). As opposed to this, if stepping up melt throughput to 20 kg/h, the content of residual monomers fails to fall below approx. 4 wt. %. In [4, 5], for example, more process parameters are discussed as to their effects.

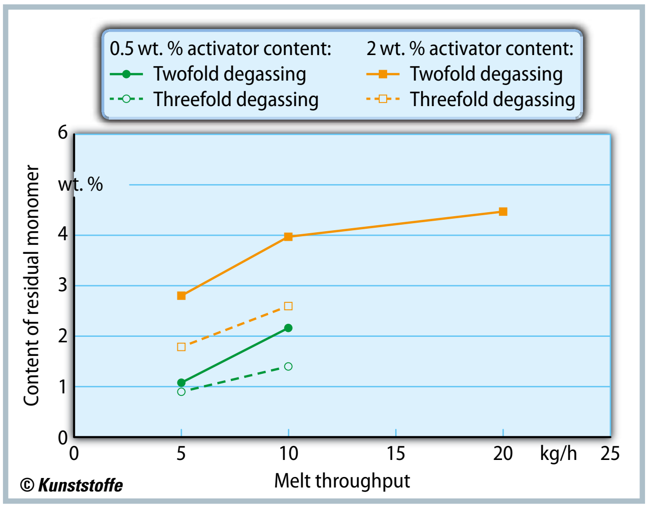

Fig. 4. Contents of residual monomer related to melt throughputs with two or three stages of vacuum degassing for different contents of activator

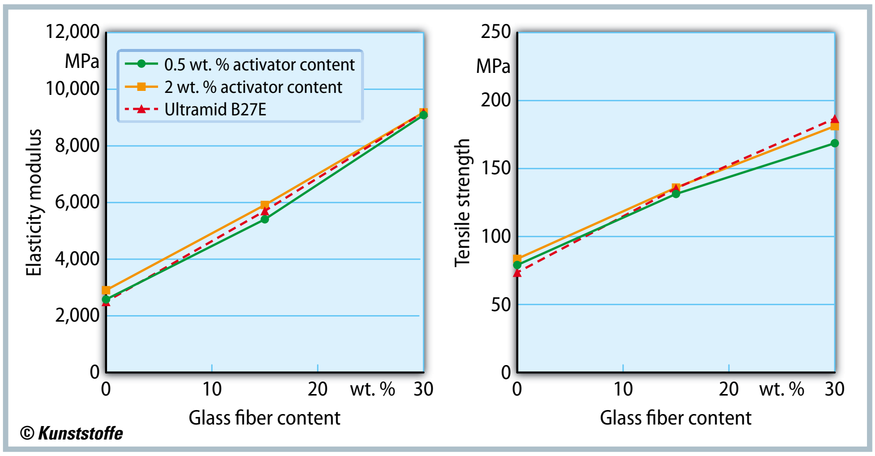

Fig. 5. Mechanical properties of directly compounded PA6/glass fiber compounds as compared to those of compounds based on commercial materials

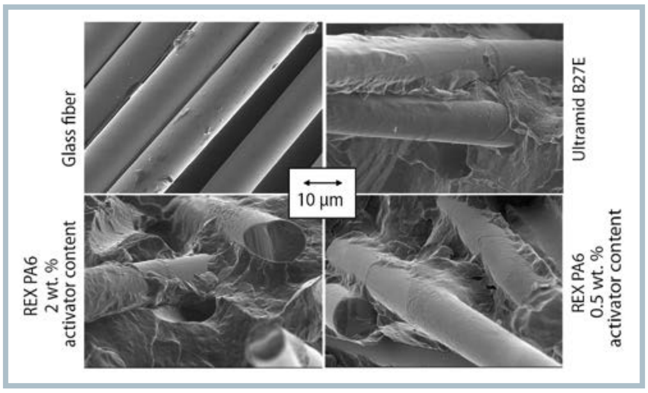

Fig. 6. Fracture surface analysis conducted by scanning electron microscopy on the compounds with 30 wt. % of glass fibers (figures: Institute of Plastics Processing (IKV) at RWTH Aachen University)

Mechanical Properties

Based on the findings of residual monomer degassing, PA6/glass fiber compounds are produced by direct compounding using a three-stage degassing unit. Without any additional intermediate steps, the compounds are processed by injection molding to manufacture tensile bars, which are then submitted to mechanical testing. HP3610 grade glass fibers (manufacturer: PPG Industries Fiber Glass BV, Hoogezand, The Netherlands) are used. The materials are compared to compounds based on hydrolytically polymerized PA6 materials (grade: Ultramid B27E, manufacturer: BASF SE, Ludwigshafen, Germany), which are produced with the production equipment and process parameters unchanged.

Figure 5 shows that stiffness and strength increase as glass fiber content is stepped up. Considering stiffness, there is hardly any difference between the directly compounded materials and the reference compound. In an unfilled state, the directly compounded materials show slightly higher values of stiffness and strength. Thus, combining polymerization to multistage vacuum degassing, the processor obtains a PA6 with a low content of residual monomers. Considering mechanical properties, this material is perfectly comparable to commercially available PA6. Only with high fiber contents do directly compounded materials show slightly deteriorated stiffness values. Especially PA6 compounds with a 0.5 wt. % activator content show lower stiffnesses, if containing 30 wt. % of fibers. Microscopic examinations of the fracture surfaces of various compounds show no visible differences concerning the degree of fiber wetting with matrix material (**Fig. 6**).

Due to the high melt temperatures prevailing in the process, the sizing of the used glass fibers transferring the stress between fiber and matrix can be assumed to degrade thermally, in part. Scientific literature describes thermal degradation of the glass fiber sizing at temperatures above 300 °C, which leads to reduction in the attainable strength of the material produced [6]. Additionally, one must assume that the sizing of the glass fibers employed does not perfectly fit anionically polymerized PA6. In this area, there is a large potential for development, which may help improve mechanical properties.

Conclusion

By applying a multi-stage process for residual monomer degassing in reactive extrusion, manufacturers are able to produce PA6/glass fiber compounds that can be processed directly and without any intermediate stages by, e. g., injection molding. The final mechanical properties of the directly compounded materials are similar to those of commercial compounds. The process developed also allows for other fillers or reinforcing materials to be incorporated. This is how, on a monomer basis, the processor can manufacture a wide variety of different PA6 compounds. ■