

Thermoplastic Wet Filament Winding

Modification of the Wet Winding Process for In-Situ Polymerizing Thermoplastics

So far, the classic wet winding process has basically been limited to thermosetting resin systems. Now, it has been demonstrated that in principle it is also feasible with in-situ polymerizing thermoplastics. Due to the sensitive response of the chemical reaction to the various process influences, the challenge lies in the machine modifications and the accurate adjustment of the process window.

Wound rotationally symmetric fiber-reinforced plastic (FRP) structures are, for example, used in pipelines for corrosive media, mandrels in the paper industry or sports equipment such as ski sticks and sailing masts. The arguments for using FRP are, in addition to the corrosion resistance, the adjustable properties as well as the lightweight construction potential. In the classic wet winding process, it is state of the art to use thermosetting resin systems. In many applications, for example in the automotive sector (tanks, drive shafts, springs), the use of thermoplastic resin systems would be an advantage because they can be re-shaped, welded and melted, and they have in general a higher impact resistance. Unlike the usual melt processing, thermoplastics can also be polymerized during the process (in-situ). This is done by processing low-viscosity monomer components that enable a good and fast impregnation of the reinforcement fibers. However, the processing of in-situ polymerizing thermoplastics in the winding process requires an extensive modification of the filament winding equipment and a modified process control. These aspects were investigated at the Institute of Plastics Processing (IKV) at RWTH Aachen University using the example of in-situ polymerizing polyamide 6 (PA6).

Low Viscosity Requires Special Equipment

In the wet winding process, the rovings are pulled from a creel into an open impregnating bath where they are impreg-

nated with the thermosetting resin. Typical pulling speeds range from 1 to 2 m/s. Through the moving feed eye, the roving is positioned along the rotating mandrel. The whole procedure typically takes

tems, the in-situ reaction of PA is influenced by environmental conditions (humidity, oxygen) and can even be terminated. The temperature as well as the mixing ratio of the reactants must be ad-

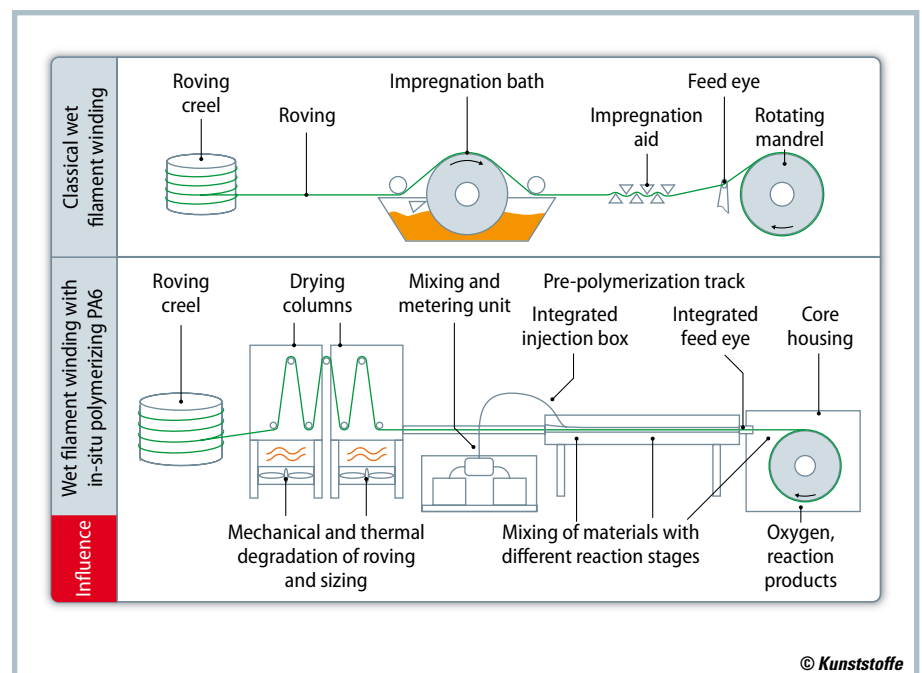


Fig. 1. Principle of wet filament winding with a thermoset resin system and in-situ polymerizing thermoplastic (source: IKV)

place in the open, without any protection from the environment. After the winding process, the wet (uncured) part is heated up in an oven to activate the crosslinking reaction and finally cured [1].

There are two main challenges when wet winding with an in-situ polymerizing PA [2–7]. Unlike thermosetting resin sys-

tems, the in-situ reaction of PA is influenced by environmental conditions (humidity, oxygen) and can even be terminated. The temperature as well as the mixing ratio of the reactants must be ad-

low enough to allow the newly wound layers to connect to the existing ones. Because the polymerization reaction cannot be interrupted, it has to be completed during the winding process.

Environmental Influences Have a Vital Impact

To overcome these challenges, a special plant engineering was developed for the used resin system (type: Instant Blend, manufacturer: Lanxess AG, Cologne, Germany) (Figs. 1 and 2). For this purpose, the resin system was first examined to analyze its processing properties with regard to tolerable environmental influences, viscosity profile and reaction time. It was confirmed that the reaction conditions have to be fulfilled without any environmental influences (humidity, oxygen). In addition, it was shown that the pre-polymerization time of one minute before winding is essential, so that the viscosity can be raised to a few pascal seconds to prevent any of the resin from dripping off. The necessary pre-reaction in a closed pre-polymerization track limits the roving speed to a maximum of 1.1 m/min, because the length of the pre-polymerization track is limited by the resultant friction.

To ensure continuous protection from environmental influences as well as a constant temperature, use was made of a roving conditioning system, a closed guide for the roving and resin system, and a temperature-controlled housing for the winding core. For conditioning, the rovings are pulled through two drying columns with multiple direction

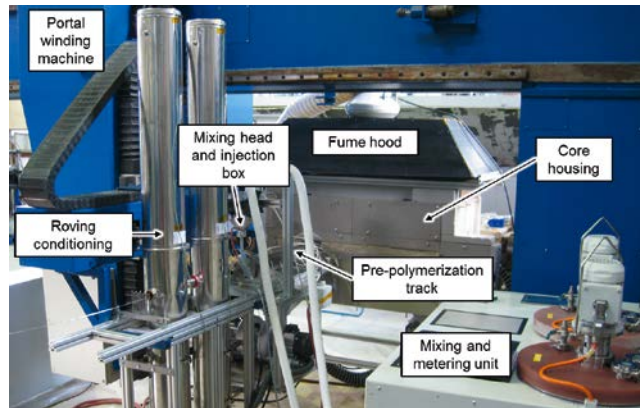


Fig. 2. Developed equipment for processing in-situ polymerizing polyamide 6 (© IKV)

changes, thereby covering a distance of approx. 20 m in hot air of 160°C (dwell time: minimum 18 min). The open impregnating bath was replaced by a closed injection box, in which the resin system is injected on demand by a mixing and metering unit (type: MarMax 122B, manufacturer: Mahr Metering Systems GmbH, Göttingen, Germany) from two inert reservoirs. The pre-polymerization track, which is similar to a pultrusion die, is positioned after the injection box. To ensure that the resin system does not drip off at low roving speeds and low temperatures, preliminary investigations regarding the viscosity development of the resin system were made and the pre-polymerization track length was set at 700 mm.

The temperature-controlled housing of the winding core is a circulating air oven, additionally inerted with nitrogen. To deal with any leaking reaction products, an extractor hood was also installed.

Through the combination of roving conditioning, pre-polymerization track and core housing, the installed equip-

ment enables the processing of in-situ polymerizing thermoplastics in the winding process. Due to the principle of the process, various influences have an effect on the polymerization reaction. Firstly, the roving sizing (type: Tufrov 4517, manufacturer: PPG Industries Fiber Glass by, Hoogezaand, Netherlands), which has been optimized for the in-situ polymerization of PA6, can be damaged by the mechanical and thermal stress. Exposed acidic hydroxy groups of the glass fiber can impede the reaction [8]. Furthermore, materials with different reaction progress become mixed up in the pre-polymerization track and on the winding core. In the pre-polymerization track, this happens through accumulation of material on the walls and on the winding core through the application of new layers onto the existing ones. This disturbs the stoichiometric mixing ratio of the reaction. Additionally, the reaction can be influenced by atmospheric oxygen (pulled in with the rovings) and reaction by-products concentrated in the core housing. »

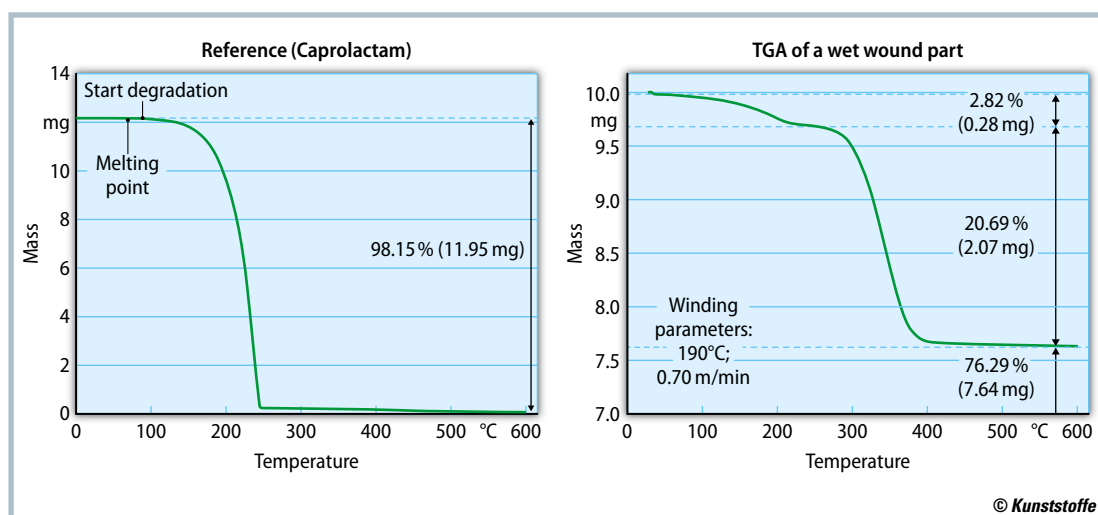
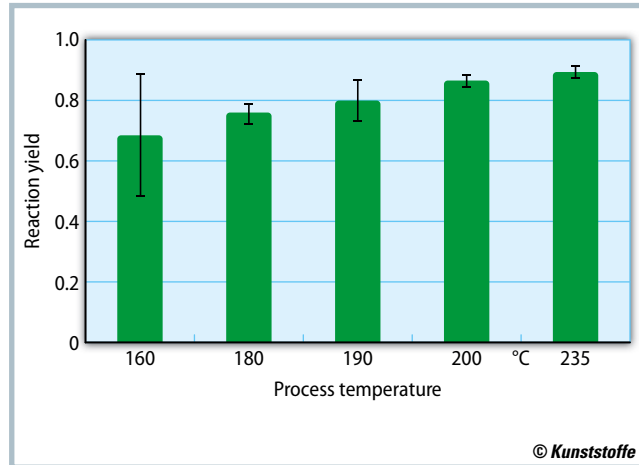


Fig. 3. Exemplary diagrams of the thermogravimetric analysis (TGA)

(source: IKV)

Fig. 4. Reaction yields depending on the process temperature (source: IKV)



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Acknowledgments

The research project 18077 N of the Forschungsvereinigung Kunststoffverarbeitung has been sponsored as part of the "Industrielle Gemeinschaftsforschung und -entwicklung (IGF)" by the German Federal Ministry of Economics and Energy (BMWi) due to an enactment of the German Bundestag through the AiF. We would like to extend our thanks to all organizations mentioned.

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Due to these influences, the reaction yield is likely to be lower than generally required (98%). However, the hypothesis exists that the negative influence is reduced when the exposure time of the roving to the interfering influences is shortened by a quicker reaction. Therefore, a subject of the investigation is to find out how the winding process with in-situ polymerizing polyamide can be performed to achieve higher reaction yields.

Analysis of the Developed Process

To analyze the process, hoop layers were wound onto a tubular core (diameter: 27 mm). The reaction temperatures (same temperatures in the pre-polymerization track and the temperature-controlled core housing) were varied between 160°C and 235°C to accelerate the reaction thermally (stages: 160°C; 180°C; 190°C; 200°C; 235°C). The roving speed was held steady at 0.7 m/min.

The reaction yield is determined for every test sample by three individual thermogravimetric analyses (TGA). Mass changes due to degradation and evaporation as a function of time and temperature can be determined with the TGA [9]. The test samples were dried for 14 hours at 65°C in a convection oven before testing. After that, they were heated at a rate of 20 K/min and the weight loss was measured (device type: TGA/DSC 3+, manufacturer: Mettler-Toledo Intl. Inc., Columbus, OH/USA). The reference used here was an un-reacted caprolactam reaction mixture (Fig. 3 left). A homogeneous degradation behavior of the caprolactam up to a temperature of around 240°C is

recognizable. The residual degradation may be caused by the activator or the catalyst. On the right in the picture is a TGA curve of a test sample (parameters: 190°C; 0.7 m/min). The curve shows two different degradation stages. The first one (up to 240°C), like the left-hand picture, can be related to the residual caprolactam monomer in the test sample. The proportion here is 2.8% of the total mass or 11.9% of the resin mass. The second stage (up to 500°C) shows the proportion of mass of the reacted PA6, here 20.7% or 88.1% related to the resin mass. The remaining mass, here 76.3% of the total mass, is the mass proportion of the glass fiber.

Figure 4 illustrates the reaction yield of all test samples as a function of the reaction temperature. The expected trend, that increasing the temperature would lead to an increased yield, was confirmed. This connection was found here for the first time for in-situ polymerizing PA6. In casting processes or reactive extrusion, it is common for the reaction yield to drop when increasing the temperature [2]. This fact that, despite this general material characteristic, the reaction yield is increased by raising the temperature in the winding process, proves the negative environmental influences.

The hypothesis that the negative environmental influences can be reduced by thermally accelerating the reaction was thus proved. However, reaction yields were low, ranging from 68% to 92%.

Conclusion and Outlook

The developed equipment basically enables the wet winding process with in-situ polymerizing PA6. However, the aimed reaction yield of over 98% (less than 2% residual monomer) was not reached, as the process parameters could not be optimized to fully compensate the environmental influences on the process. Furthermore, the roving speed is low (maximum 1.1 m/min) which would lead to long cycle times.

Future developments should focus on higher roving speeds and reaction yields. Approaches for increasing the reaction yield, are a more gentle roving drying system, optimization of the pre-polymerization track to avoid accumulation on the walls, and further measures to protect the process from environmental influences. ■