SPEZIAL

Polyurethane (PU) as alternative matrix system in pultruded composite profiles

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Introduction

Composites with thermoset matrix systems are established as lightweight construction material for structural parts with high weight-specific mechanical properties. The reinforcement fibres are oriented and high fibre volume contents (> 50 %) are used. An established manufacturing technique for the production of composite profiles is the pultrusion process. A wide range of applications results by custom-designed properties of pultruded parts. For example pultruded parts are used as load-bearing structures in the building sector or lining elements in the transportation industry [1]. The advantages of the pultrusion process are high laminate qualities, a high degree of automation and an eminent economic efficiency.

A further reduction of the production costs can be achieved by the use of alternative matrix systems with comparable material properties by reduced raw material costs and increased processing speeds. By the restricted reactivity of the most commonly used matrix systems the processing speeds are limited.

Principles of the pultrusion process

Manufacturing lines of composite parts with thermoset matrix systems always consist of the following processing steps: Shaping, fibre impregnation, and curing of the matrix material. The pultrusion process unites these three processing steps in one machine (Fig. 1).

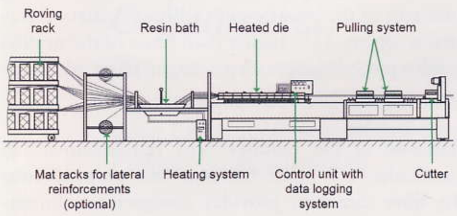

Figure 1: Draft of a pultrusion line [2]

Firstly, the fibre bundles (rovings) are drawn-off from a roving rack and guided into a resin bath. For lateral reinforcement optionally semi-finished fibre materials such as mats, fabrics or fleeces are added. In the resin bath the fibres are impregnated with the matrix material. Following the impregnated fibres are pre-shaped according to the desired distribution of the fibres in the profile. Optionally a pre-heating system is supplied. Pre-heating is necessary for profiles with high volumes to avoid large temperature gradients over the profile cross section: Large temperature gradients result in high internal stresses. Afterwards the profile is shaped by a heated die and the matrix material is cured. The cured profile passes a cooling track and is tailored by a cutter. The entire process is kept running by a pulling system, which pulls the profile continuously out of the die [1].

The pultrusion process with conventional matrix systems

Besides the fibres, the matrix material effects the properties of pultruded profiles. In particular the chemical, electrical and also thermal properties of the profile are influenced. Commonly used matrix systems in the pultrusion process with thermosets are unsaturated polyester, vinyl ester and epoxy resins. Unsaturated polyester resins find the most application fields due to the relatively low material costs. Vinyl ester resins are used in applications, which demand a higher chemical resistance. Epoxy resins are used in parts with high mechanical requirements. In addition epoxy resins have excellent chemical and heat resistance.

The essential process parameters in the pultrusion process, which determine the output and the quality of the profiles, are the temperature distribution in the die, the pultrusion line speed and the reaction kinetics of the used matrix system.

The temperature distribution in the die has to guarantee that the curing status of the thermoset matrix system assures the dimensional stability of the profile. The die temperature may not be selected too high. High die temperatures lead to extreme temperature and reaction gradients over the profile cross section. The results are high internal stresses in the finished profile. In addition early curing in the die has negative effects on the pulling forces and the stability of the process. By defining the retention time of the matrix material in the die the pultrusion line speed is a further essential parameter in the pultrusion process. Together with the die temperatures the pultrusion line speed defines the reached curing state of the matrix material. Besides the pultrusion line speed determines directly the output, which should be as high as possible for economic reasons [3].

Furthermore also the reaction kinetics of the used matrix system has a significant influence on the achievable production speed and the profile quality. Therefore possible process windows are determined by the reaction kinetics, the pultrusion line speed and the die temperature. In particular high-reactive materials are used in the pultrusion process. For example several catalysts are usually added to unsaturated polyester resins, which initiate a fast cross linking in different temperature zones of the die. In this way an effective and homogeneous cross linking over the profile cross section is possible.

Advantages and challenges pultruding PU as matrix system

An option, to increase the efficiency of the pultrusion process is the application of polyurethane (PU).

The big advantages of the use of PU in the pultrusion process are the wide-ranging variation options of the material manufacturers concerning the adaptation of the material properties such as reactivity and viscosity on the respective manufacturing process. A majority of the PU systems can be adapted within a wide range to the part requirements. For example flexible to rigid material properties are possible.

Compared with conventional matrix systems further advantages from PU are that no styrene emissions exist and, in particular when using two-component polyurethane systems (2C-PU), the high reactivity facilitates high processing speeds.

Challenges to face when processing PU are the high sensitivity of the systems in relation to humidity and the high reactivity. So in the pultrusion process with PU an extended machine technology has be used.

Machine and die technology of the pultrusion process with PU

The material-specific characteristics of PU result in different requirements in particular to the impregnation unit of the pultrusion line. Due to the comparatively high reactivity of two-component polyurethane systems an impregnation with a continuous matrix material supply has to be used. The impregnation unit has to be thermally separated from the heated die in order to prevent the curing already in the impregnation unit.

In addition a majority of PU systems tend to expand when exposed to humidity. In order to minimise the contact of the PU with the ambient air, a closed impregnation unit has to be used. To fulfil these requirements an injectionbox (Fig. 2) has been developed and integrated into the pultrusion line.

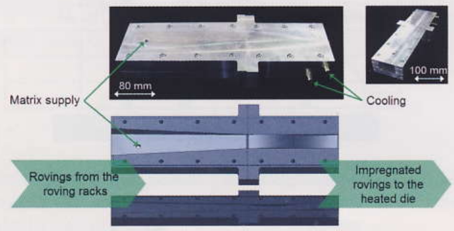

Figure 2: Injectionbox for fibre impregnation

The injectionbox is a multipart tool, in which the reinforcement fibres are impregnated with the matrix system. The fibres pass through a conical channel. The matrix material is injected through a gate in the top side of the injectionbox. A defined matrix flow rate guarantees that no surplus matrix material develops within the box. Because of the conical geometry of the impregnation area a pressure is build up within the material, by which air inside the rovings escapes to avoid the formation of voids in the profile. Directly to the injectionbox the heated die is attached. To realise the thermal separation of the injectionbox from the die a cooling system is integrated into the system.

Pultruding a one-component PU: Epoxy isocyanurate (EPIC)

As one-component PU an EPIC system was selected. The possibilities and the potentials of the pultrusion process with an EPIC system had to be demonstrated. EPIC systems are used in particular as casting resins and in different sectors for manufacturing composite parts.

The used EPIC system (Blendur®, Bayer MaterialScience AG, Leverkusen, Germany) is an epoxy-modified polyisocyanurate, which consists of 80 % diphenylmethane diisocyanate (MDI) and 20 % of epoxy resin on bisphenol A base. The one-component system is containing a thermal latent catalyst. Due to so many excellent properties EPIC is qualified for different applications. Expected properties of parts manufactured with EPIC as matrix system are:

- high glass transition temperature (TG) of approx. 300 °C,
- high thermostability,
- small thermal expansion,
- inherent flame protection,
- good chemical resistance and
- high electrical isolation properties to over 200 °C [4].

In particular the inherent flame protection and the high glass transition temperature are properties, which can be realised only by addition of cost-intensive additives with conventional matrix systems. Within the investigations at IKV process parameters for the pultrusion process were determined and optimised. Figure 3 shows the temperature distribution in the die and in the pultrudate during the pultrusion process with EPIC at a pultrusion line speed of 0.2 m/min (profile cross section: 35 x 4 mm²). Following the profiles are tempered.

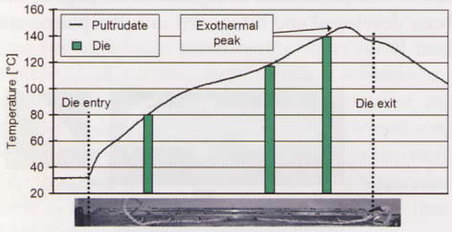

Figure 3: Temperature gradient in pultrusion die and the pultrudate during the pultrusion with EPIC (v = 0.2 m/min)

Firstly, with the thermal latent EPIC as matrix system the conventional resin bath was used for fibre impregnation. Subsequently, the resin bath was replaced by the developed injectionbox. As the images pictures of manufactured profiles in Figure 4 show, the number of voids can be reduced by using the injectionbox compared to the resin bath. In addition a more uniform arrangement of the fibres in the profile is observed, whereby a fewer number of conglomerations of matrix material exist. The occurrence of conglomerations of matrix material, which have no link to the laminate, is completely avoided during the fibre impregnation by the injectionbox.

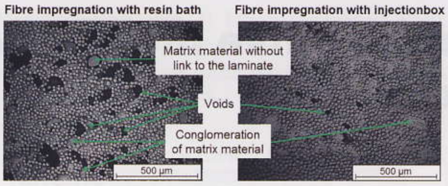

Figure 4:Comparison of the impregnation quality with different impregnation units

Pultruding a two-component PU

The pultrusion process of two-component PU is already known [5], however the use of pultruded profiles with two-component PU as matrix system is still unestablished. This is to be attributed to the fact that on the one hand an extended equipment technology is necessary and on the other hand only few reliable properties of these profiles are available. In the pultrusion process with two-component PU the employment of the injectionbox is inevitable due to the high material reactivity.

In addition the pultrusion line has to be extended by a PU metering machine. In the metering machine the raw material components polyol and isocyanate are stored in two separate tanks and delivered by metering pumps in a defined flow rate to a mixing head with a static mixer. The mixed material reaches the injectionbox by a short connection tube, in which the impregnation of the fibres takes place. In the investigations carried out at IKV a PU system was used which is optimised for the pultrusion process (Baydur Pul, Bayer MaterialScience AG, Leverkusen, Germany).

The studies at IKV showed that the used polyurethane system is relatively insensitive to changes of the process parameters as well as external influences. The process is well controllable. Pultrusion line speed up to 1.8 m/min have been realised (profile cross section: 35 x 4 mm2, Fig. 5).

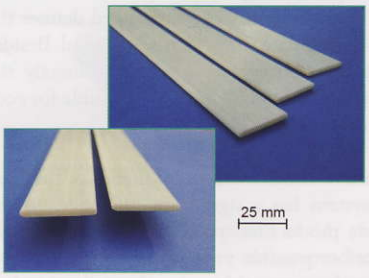

Figure 5: Pultruded PU profiles

The pultrusion with PU in comparison to the pultrusion with conventional matrix systems

To compare the pultrusion with PU to the pultrusion with conventional matrix systems, further investigations with industrially established materials were realised. In these investigations unsaturated polyester, vinyl ester and epoxy resin systems were used and the fibre impregnation was realised by using the injectionbox. The pultrusion line speed and die temperature distribution were adapted to the respective matrix system, so that profiles with cured matrix were manufactured at maximised pultrusion line speed. Maximum processing speeds of 0.3 m/min could be achieved. In all investigations, which are discussed in this article, rovings with the indication StarRov® Direct Roving 908 (Johns Manville, Denver, USA) were used.

After manufacturing the profiles with suitable processing parameters the produced profiles were mechanically characterised. The 3-point bending test was realised parallel to fibre direction according to DIN EN ISO 178 by Röchling Engineering Plastic KG, Haren, Germany (Fig. 6).

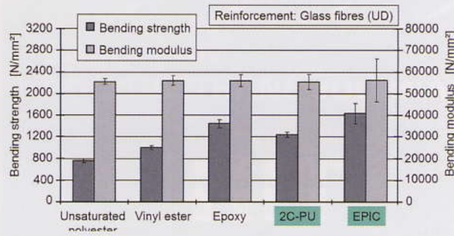

Figure 6: Results from 3-point bending test (parallel to fibre direction) according to DIN EN ISO 178

The profile stiffness parallel to fibre direction is primarily defined by the fibres. But the bending strength depends also on the strength of the matrix material and the adhesion between the matrix material and the fibres. The measured bending strength of the profiles with two-component PU as matrix system is comparable with the bending strength of the profiles with epoxy. The bending strength of the profiles with EPIC as matrix material is approx. 13 % higher than those of the profiles with epoxy, however also a larger standard deviation is registered.

Because of the unidirectional reinforcement, in particular a 3-point bending test perpendicular to fibre direction provides comparing information about the mechanical properties of the matrix systems and the adhesion between the matrix and the fibres. The 3-point bending test was realised according to DIN EN ISO 178 (Fig. 7), in which a shortened bearing distance of 25 mm was used.

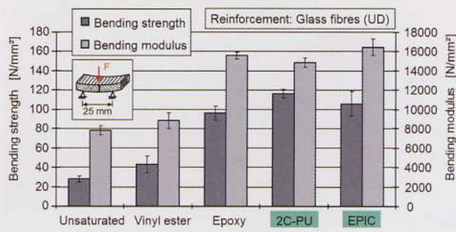

Figure 7: Results from 3-point bending test (perpendicular to fibre direction) according to DIN EN ISO 178

As Figure 7 shows, the measured bending modulus of the profiles with two-component PU and EPIC is relatively high and quite comparable with those from profiles with epoxy. The measured bending strength of the profiles with the two-component PU as matrix system is even approx. 20 % higher as that of the profiles with epoxy as matrix system.

In many applications composite parts are subjected to impact loads. In these cases a failure of these parts can be prevented by a high energy absorption capacity. To characterise the manufactured profiles the Charpy impact test was realised (Fig. 8).

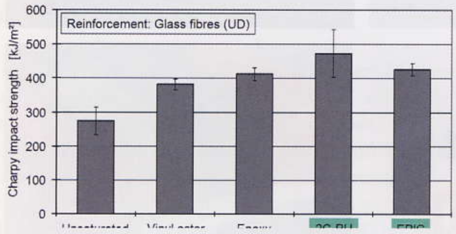

Figure 8: Results from Charpy impact test according to DIN EN ISO 179-1

The results show that the possible energy absorption capacity of two-component PU is high compared with conventional matrix systems in the pultrusion process. The results for the profiles with EPIC as matrix system are comparable with the profiles with epoxy.

Additionally to the mechanical investigations the profiles with EPIC were characterised by the dynamically mechanical analysis (DMA). The profiles are exposed to a dynamic bending load inside an oven and the storage and loss modulus are noted in dependency of the temperature. If the sample reaches the glass transition temperature of the matrix material, the loss modulus shows a maximum. For the profiles with EPIC as matrix system glass transition temperatures of 280 °C were determined.

Conclusion

Pultrusion with PU turns out as very efficient in comparison to the pultrusion with conventional matrix systems. The measured mechanical properties of manufactured profiles are comparable with the results of profiles with an epoxy resin as matrix. Furthermore the possible energy absorption capacity of two-component PU is high compared to conventional matrix systems for the pultrusion process. EPIC as matrix system facilitates production of profiles with high heat deformation resistances. Remarkable is that the achieveable pultrusion line speed with two-component PU is much higher compared to processing of conventional matrix systems. In summary the investigations show that PU in the pultrusion process possesses the potential to manufacture composite profiles with optimised properties still more efficiently.

Outlook

In future work the possibilities of adaptation of the PU characteristics to different part requirements will be examined. For example elastic or foamed composite profiles with PU as matrix system are conceivable.

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