Tailored to Reactive Polyamide 6

Thermoplastic Resin Transfer Molding (T-RTM). The T-RTM process has been successfully applied as a B-pillar reinforcement made from a continuous fiber-reinforced plastic, utilizing a low-viscosity caprolactam system. This was done in cooperation among the company research team at Volkswagen AG, BASF SE and Krauss-Maffei Technologies. This production variant borrows from current RTM processing technologies and can be used to produce thermoplastic FRP parts for automotive applications economically.

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There are two dominant motives for utilizing fiber-reinforced plastics in automobiles: for one thing, its high directional stiffness and strength in concert with low density render this class of materials eminently suitable for lightweight applications. This is especially interesting for car body construction, since lightening the undercarriage can enable reductions in tank volume and engine size, thereby achieving further secondary weight reduction effects without impairing performance. In this way, a valuable contribution can be made toward fulfilling the goals of further emission reduction in future vehicles, to meet tightening legislative requirements, and the conservation of needed resources.

For another thing, the desire for individual mobility has led to a wider variety of models and shorter model cycle changes, the result of which is smaller numbers per model [1]. For this reason, one-time occurring investments are becoming more important. On the other hand, the costs incurred for each part, such as production and material costs, continue to be sure enormously important, but they no longer totally dominate cost distribution. If a lower piece number can be assumed for many derivatives, the relatively expensive FRP’s still represent an economical alternative, to the extent they can save considerable costs of investment in production facilities, tools and press lines.

Processes suitable for automobile mass production have to fulfill demands for high and reproducible part quality in ad-
tion to economic requirements. Among the FRP production methods still characterized by manual activities, Resin Transfer Molding (RTM) can well be regarded as a robust production process, since it has potential for a high degree of automation. In the previously used RTM processes, thermosetting matrix systems, usually epoxy resin, were used exclusively.

By contrast with thermoset systems, thermoplastic matrix systems have the advantages of better recyclability, as well as the capability for subsequent reshaping and weldability, resulting in more advantageous overall efficiency. Thermoplastic matrix systems have not been utilized by conventional RTM processes, since their relatively high viscosity in a molten state practically prevents semi-finished fiber parts from soaking pore-free with acceptable process parameters. Combining the advantages of thermoplastics with those of the RTM process.

**The Thermoplastic RTM Process**

The schematic sequence of the T-RTM process by reactive polyamide does not differ significantly at first glance from the classic RTM process (Fig. 1). The process chain begins with the 2-D cutting of a semi-finished textile reinforcement fabric. In our example of a B-pillar reinforcement, a glass fiber fabric was used whose special finish is suitable for wetting with caprolactam while it ensures good fiber-matrix adhesion in the final part. The textile layup can thus be adapted to the particular loads on the final FRP part via both its layer structure with variously oriented individual layers as well as via the semi-finished textile in the individual layer tailored to its final shape as a B-pillar reinforcement in the last production step.

To perform the T-RTM process, a slightly modified conventional RTM mold was used on an existing 1,000 t press at the Volkswagen company’s FRP testing plant in Wolfsburg (Fig. 2). The first successful production trials had already taken place when the injection machine was put in service at KraussMaffei’s pilot plant in Munich.

The reactive system consisting of the original caprolactam as well as an activator or catalyst and additional additives in the form of two ready-mixed components from BASF is fed at room temperature into the heated container of the dosing system. Above a temperature of approx. 70°C, the caprolactam melts and has a watery viscosity. By themselves, both liquid components are hardly reac-

These disadvantages in terms of production technology could be avoided by using a reactive thermoplastic matrix system based on polyamides made by anionic polymerization. The matrix system also known by the concept of cast or reactive polyamide exhibits very low viscosity prior to polymerization in a molten state, clearly lower than that of commercial epoxy resin systems. Once the fiber is thoroughly soaked, the reactive caprolactam system polymerizes to a polyamide 6 (PA6) within approx. 2 to 3 min in an isothermally tempered mold. By utilizing reactive polyamide as a matrix system, this processing technology puts a thermoplastic RTM process (T-RTM process [2, 3]) to use, thus enabling thermoplastic FRP parts to be manufactured at low injection pressures in short cycle times and

**Fig. 2. T-RTM Testing setup at the FRP pilot plant at Volkswagen company research**

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closed process concept of the T-RTM process ensures moisture-free injection of the caprolactam system.

As shown in Figure 3, the monomer’s low viscosity enables excellent fiber wetting at an injection temperature of approx. 100°C even in complex geometries. Taking the B-pillar reinforcement with wall thicknesses ranging from 6.3 to 12 mm as our example, fiber volume contents of 54 % to 58 % were achieved in a pore-free laminate. Injection and curing required less than 5 min. Current experiments ought to achieve further shortening to less than 3 min.

The B-pillar Reinforcement Part

The B-pillar reinforcement selected for the prototype is a thick-walled structural part produced in mid-range numbers for the North American market that serves to absorb energy in so-called pole crash tests. Both the geometry and great wall thickness of the part presented a special challenge for the RTM process, whereby the use of the reactive polyamide system turned out to be quite advantageous.

The B-pillar reinforcement used in series production at Volkswagen is made from high-strength steel. By using glass fiber-reinforced plastic (GFRP), part weight could be reduced by 36 %. The geometry of the part was modified to conform to fiber composite construction. The GFRP variant of the B-pillar reinforcement is glued to the metal interior section of the B-pillar (Fig. 4), thereby representing potential application for FRP’s in light-weight car body construction.

Material

The anionic polymerization of caprolactam to polyamide 6 in the presence of activators and catalysts was first described in the literature in the nineteen-fifties [4, 5]. By way of contrast with hydrolytic polymerization, the standard technology in large-scale production processing, the polymerization reaction is completed within a few minutes instead of 24 hours. Anionic lactam polymerization is currently applied industrially in rotomolding, or in cast polyamide for the production of semi-finished profiles, cable car rolls and similar parts requiring high toughness characteristics and abrasion resistance. The chemistry of anionic lactam polymerization is very interesting for the production of FRP parts, since for one thing caprolactam’s polarity enables it to dissolve numerous additives and, for another, its low viscosity makes it well suited for impregnating textile structures. As a leading manufacturer of caprolactam and supplier of engineering plastics, BASF has been involved in research to produce thermoplastic composite mate-

Fig. 3. Micrographs of a thermoplastic GFRP B-pillar reinforcement

Fig. 4. Installation situation of the B-pillar reinforcement

rial by anionic lactam polymerization for more than three years. Analogous to its existing portfolio of polyamide 6 compounds (Ultramid B), BASF has developed a so-called chemical toolbox.

This toolbox enables BASF to provide formulations that contain not only the activator or catalyst, but also the corresponding heat stabilization, internal release agent, or a toughness modifier and a reactivity tuned to the process. Polymerization typically takes place in approx. 2–3 min for high-molecular PA6 at 140–160°C.
An additional challenge is presented by the compatibility of fiber layers with the polymerization reaction, so that the chemical reaction is not interrupted. Together with manufacturers of glass and carbon fibers, BASF researchers are currently developing appropriate facings in order to be able to supply a complete system solution consisting of a formulated reactive system and a compatible semi-finished textile. The reactive system consists of a so-called A-component, which contains the activator in addition to the caprolactam, and a B-component with the catalyst in caprolactam. Both components will be supplied in the form of easy-to-handle bins, melted in an RTM injection machine at 90–110°C and mixable at the ideal ratio of 1:1.

The resulting FRP part exhibits an excellent stiffness/toughness relationship combined with high heat stability. Further advantages of this in-situ produced thermoplastic composite material include the potential for subsequent reworking, welding and recyclability.

BASF’s goal is to supply the processor with a complete solution consisting not only of a pre-tuned reactive system together with the semi-finished textile, but also including support for configuring and producing the part. For this, extensive materials tests are being performed on composite materials in order to support users with simulation for part design.

**Plant Technology/ Dosing System**

Thanks to their extensive experience in this area since the mid-eighties, KraussMaffei was able to contribute the dosing system required for the project (Fig. 6). Under the previous process designation, NY-RIM, meanwhile T-RTM, the Munich-based company has since then supplied dozens of systems for the reactive processing of caprolactam.

The trick to the T-RTM process lies in plant technology tailored precisely to the reactive processing of caprolactam. KraussMaffei’s mixing and dosing system is, therefore, equipped with a special mixing head, powerful axial piston pumps as well as constant electrical tempering.

Based on this know-how, the NY-RIM mixing head was completely redeveloped for the T-RTM process in addition to a new dosing machine designed especially for it. Whereas very large mixing heads were required for processing caprolactam, the mixing heads used today have a very compact construction. They are heated electrically, are theoretically suitable at processing temperatures up to 160°C and cover an output range of 10 to 200 g/s. These mixing heads permit a third component to be admixed. That can be additional additives, e.g., colored caprolactam, additional activators or catalysts.

The dosing system pumps also have to be adapted to the properties of caprolactam, e.g., the material’s low viscosity. Since KraussMaffei has itself developed the axial piston pumps used, they are perfectly attuned to the requirements of the T-RTM process. Pump power is transferred via a sealless integrated magnetic coupling. In addition, those pump parts that come in contact with caprolactam are protected by special measures against corrosion. This clearly leads to longer service life. Moreover, the axial piston pumps feature compact construction and very precise dosing.

Constantly heated runners have proven themselves: the caprolactam in the T-RTM dosing system is transported in them from the day tank to the mixing head. Coupling pieces are equipped with heater cartridges to avoid cold bridges. This optimized heating concept insures that the caprolactam temperature never falls below melting temperature and that the material thereby remains in a molten state in all zones. If there were cold bridges, the material could solidify and form plugs in the runners.

Due to its chemical structure, molten caprolactam tends to absorb ambient atmospheric moisture. As a process relevant measure, the day tanks are held under vacuum or pre-treated with nitrogen. To keep the caprolactam from coming in contact with moisture, e.g., from ambient air, the mold is also rinsed with nitrogen prior to being filled with the material.

The T-RTM dosing system together with the described combination of innovative processing technology, corresponding plant preparation and process know-how formed the basis for a high process consistency that served all project partners well.
Conclusion

Within the framework of a cooperative project between company research at Volkswagen AG, BASF SE and Krauss-Maffei Technologies GmbH, the T-RTM process was developed using a B-pillar reinforcement as the prototype at the Volkswagen Corporation’s pilot plant in Wolfsburg. The parts were manufactured by injecting a low-viscosity, reactive caprolactam system into a closed mold lined with a layer structure consisting of semi-finished continuous fiber-reinforced textiles in which it polymerizes to a polyamide 6.

Extensive materials development was required for the caprolactam system used in the T-RTM process so that corresponding formulations could be supplied. These also contain, in addition to the required activator and catalyst, a number of additives and fillers in order to form matrix systems appropriate to subsequent use purposes. Moreover, these caprolactam systems are compatible with the semi-finished textiles, facings and binders used. For uninterrupted processing, a dosing system with a suitable dosing head has to be used that is specially adapted for processing this extremely low-viscosity system.

It could be shown that parts can be manufactured with good laminar quality in the T–RTM process when appropriate fiber-matrix systems as well as suitable plant technology are used. The process thus demonstrates its potential for producing thermoplastic FRP parts for automotive applications economically.

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