The fiber-reinforced polyamide kayak was designed by Haluzka. It was produced by in-situ polymerization in a vacuum infusion process (figure: BASF)

Resins and Reactive Systems

Fiber Reinforced Plastics Finally Ready for Series Production

Epoxy resins and polyurethanes are outdoing each other with ever shorter cure times. There is downright competition as to which of them will serve in the large series of automotive production. In-situ polymerization remains an exciting issue. Most types of composites now sail in calmer waters, though. Ecological aspects and resistance to flames are the outstanding features of the new developments.

German composite producers see the general economic climate and their own economic situation as very favorable at present. This was the outcome of the latest market survey conducted in 2013 by the economic association Composites Germany, Frankfurt [1], which was constituted by four leading organizations of the German fiber composite industry. Carbon fiber-reinforced plastics (CFRP) are seen as the main driving force of growth in the future (**Fig. 1**) with increase expected in the automotive and aviation sectors.

The market of thermoset glass fiber-reinforced plastics (GFRP), with its approx. 900 kt production volume in Europe, has largely stabilized in recent years [2]. There are decreases in certain applications and processing techniques, increases in other areas make up for, though. The segments of transport and construction consume a third of the total production volume, each; other sales markets are E&E as well as sports and leisure.

With global demand for GFRP at only 59 kt in 2011, the market grows at an annual rate above 13 %, at present, though. Consumption is thus expected to reach 208 kt in 2020. Constituting 23 % of the demand, wind power is far ahead of other applications, while aviation is the number one industry in terms of turnovers [3].

Flame Protection and Ecology

Increased application of structural parts of unsaturated polyester resins in public transport has led to new developments to improve fire protection. The usual mineral additives such as aluminum trihydroxide or magnesium hydroxide increase the viscosities of polyester and vinyl ester resins so significantly that processing by resin transfer molding (RTM) or vacuum infusion, for example, is usually impossible. In addition, highly rigid textile nonwoven fabrics can hardly be soaked. A new concept of Büfa Composite Systems GmbH & Co. KG, Rastede, Germany, thus comprises

	Brookfield resin viscosity [mPas]	Heat release rate according to ISO 5660-2 [kW/m²]	Tensile strength 4 mm-laminate [N/mm²]
UP-ATH highly filled, glass mat reinforced	2,300–3,000	70 (= HL2)	88
UP-ATH moderately filled + intumescent gel coat, glass fabric reinforced	700–1,500	65 (= HL2)	204
VE LEO, reinforced with nonwoven glass fabric	240–340	45 (= HL3)	554

Table 1. The flame retardance concept of LEO (Lightweight with Extreme Opportunities) enables the production of highly-rigid fiber-reinforced plastics in injection or infusion processes (figure: BÜFA)

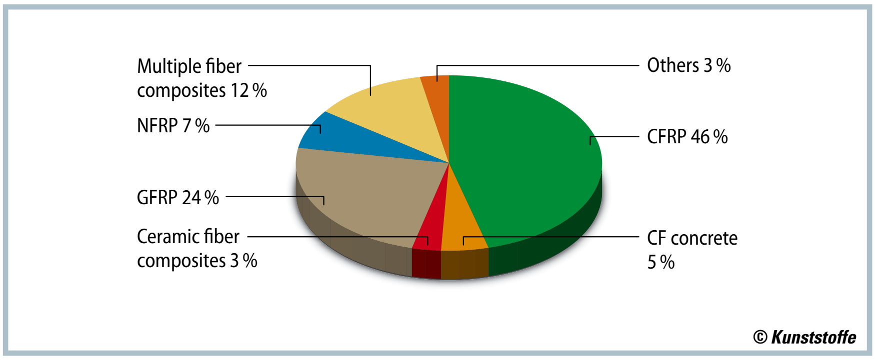

Fig. 1. Driving forces in the area of composites, as per 2014 (figure: Composites Germany)

several stages of flame protection, without severely restricting the flowability of the matrix. First, a protection layer, i.e. a gel coat or top coat with intumescent properties, are applied. Second, the vinyl ester resin system itself is modified. Glass or carbon fibers are finally applied as multi-axial reinforcing materials, which also feature flame-retardant properties [4]. This is how the product complies with a large number of national and European fire standards for the shipbuilding, construction and transport sectors (**Table 1**).

In former times, an "ecological approach" in polyester resin processing used to mean reducing styrene emissions, most of all. Today, all leading suppliers also offer resins that are entirely free of styrene [5–8]. In addition, unsaturated polyesters on a partially vegetal basis are available.

As an alternative to Cobaltoctoat, which is currently monitored by the European Chemicals Agency, Umicor in Brussels, Belgium [9] offers an accelerator with the cobalt embedded in a polymer structure. The BluCure accelerator by Akzo Nobel N.V. in Amsterdam, Netherlands, is even entirely free of cobalt (**Fig. 2**) [10].

Novelties from Acrylate Chemistry

At present, there is a trend towards monomers that can be used as a basis for reactive thermoplastic fiber composite materials, because they allow flexible processing and balanced component features, at the same time. Arkema in Colombes, France, developed a new product line of acrylate chemicals designed for thermoplastic composites [11]. The transparent, low-viscous material named Elium can be processed in a way similar to polyester resin processing. The material is especially well suited for large components with low investment for tools (**Fig. 3**). According to tensile tests, the material's properties are comparable to those of epoxy resins used for analogue applications, but it can easily be formed, welded and melted.

The portfolio comprises liquid systems, mainly for Light-RTM and vacuum infusion applications. With placing a thermoformed carrier of, e.g., ABS/PMMA (acrylonitrile butadiene styrene/polymethyl methacrylate) into the mold prior to injection molding, varnish-free components with class-A surfaces can be produced.

Large Market of Wind Power Plants

For several years, all over Europe, capacities for electric energy from wind power plants have grown by an annual 10 GW. At least – wind in Europe now supplies electric energy for approx. 60 million households. This sets up a huge sales mar- »

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Fig. 2. The Pastoe Low Chair 03 consists of a flax fiber reinforced polyester resin entirely free of cobalt, with an accelerator on a BluCure basis (figure: DSM/Akzo Nobel/NPSP Composieten)

ket for epoxy resins and reinforcing fibers. Modular systems of epoxy resin matrices of different hardnesses or with latent filler systems are established applications of fiber-reinforced epoxy resins for rotor blades. Partial application of CFRP can handle the increased forces acting upon larger offshore blades. Root rings can be generated in a winding process, even at large dimensions. This is now possible thanks to an epoxy resin with long open times, developed by BASF SE, Ludwigshafen, Germany [12] (**Fig. 4**).

Cure Speed Below the 2-Minute-Mark

Polyester and epoxy resin components made in the RTM process have been applied for some decades at small series for racing and utility vehicles. Visible and structural components, components for the passenger department and roofs are some of the typical applications. Traditionally, the period of injection and cure can well be around an hour, which is no feasible option for large numbers.

Thanks to new epoxy resin systems and to the newly developed high-pressure RTM process, continuous fiber-reinforced epoxy resin composites have made their way into the large series production of automotive parts, in recent years. This is how most carbon fiber-reinforced components, such as side panels, base trays, bumpers and crash boxes can be produced more than 100,000 times every year.

The various raw material suppliers recently adapted their basic thermolatent special types of epoxy resins, i.e. the brands of Baxxodur, Voraforce, Epikote and Araldite, to fit fast curing [12–15]. Viscosities are below 200 mPas, which is a value extraordinarily low. This makes it possible to soak the semi-finished fiber product within a period clearly below one minute, subject to the respective component; cure speed is about to fall below the 2-minute mark (**Fig. 5**). Glass transition temperature is usually 120 °C, approximately.

Another innovative process to manufacture components with continuous fiber reinforcement, is the compression molding of impregnated semi-finished fiber products or preforms. Cycle times are also low in this process. The reinforcing material is added a thermolatent resin/hardener system, which is then compacted and hardened in the mold. Some types can be sprayed upon the fibers in a liquid form, while some are available as a meltable powder to be sprinkled [15, 16].

Fig. 3. In-situ acrylate enables infusion at ambient temperature and yields damage-resistant components: CFRP boat with a thermoplastic matrix (figure: Arkema/Canoe)

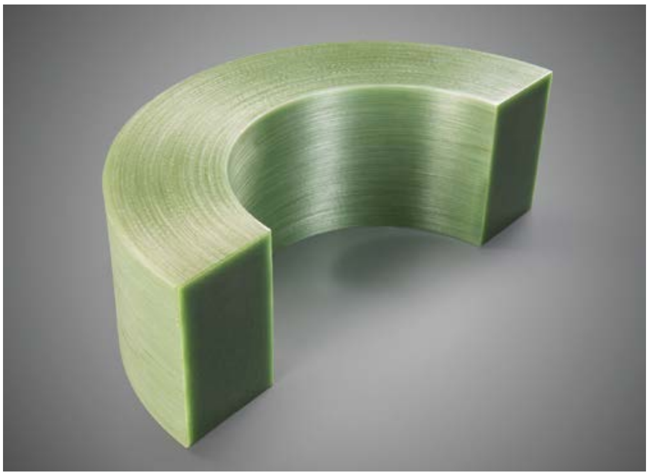

Fig. 4. Segment of a GFRP root ring of 12 cm thickness, designed for rotor blades (figure: BASF)

Matrix Resins on a Polyurethane Basis

Matrix resins on a polyurethane basis are entering industrial application at enormous speed [12, 15, 17]. They can be processed by all techniques usually applied to manufacture high-performance fiber-reinforced plastics, featuring outstanding strength of components and excellent resistance to damage. Starting from the first types of RTM polyurethanes, glass transition temperature could be increased, too. Not only does this enable high temperatures of use, but also demolding at an earlier state in the manufacturing process.

The two-component liquid systems harden with catalysts of a snap cure mechanism, which makes open time widely adjustable and which reduces cure time significantly. Their maximum initial viscosities are 100 to 200 mPas – at processing temperatures of approx. 80 to 120 °C, which is clearly below the values of conventional reactive resins. In this way, thanks to low flow resistance in the mold, large-surface multi-layer semi-finished fiber products can be soaked effectively without any major fiber displacement. This also implies low pressures during injection, which enables high surface qualities. New developments of materials and processes are therefore focused on surface technology, in particular.

Henkel AG & Co. KgaA in Düsseldorf, Germany, even offers the second generation of a commercial polyurethane matrix resin. Its internal release agent provides for good demolding, and is also adapted to a PU varnishing system of Rühl AG & Co. in Friedrichsdorf, Germany. This filler varnish is injected onto the cured component in a second step of the RTM process, to equalize uneven surfaces that may exist. Subsequent final varnishing then yields extraordinarily high-quality surfaces, without further treatment. **Figure 6, left**, presents a varnished CFRP roof segment with the Loctite Max 3 polyurethane matrix resin. »

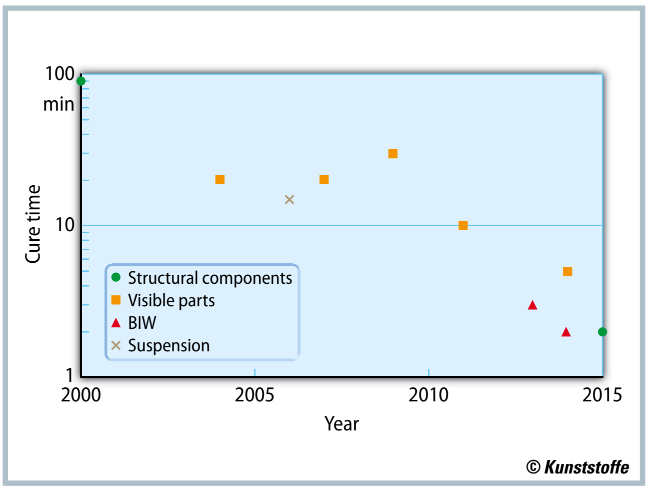

Fig. 5. Cure times of epoxy resin hardener systems for automotive components were diminished significantly within recent years (figure: Momentive)

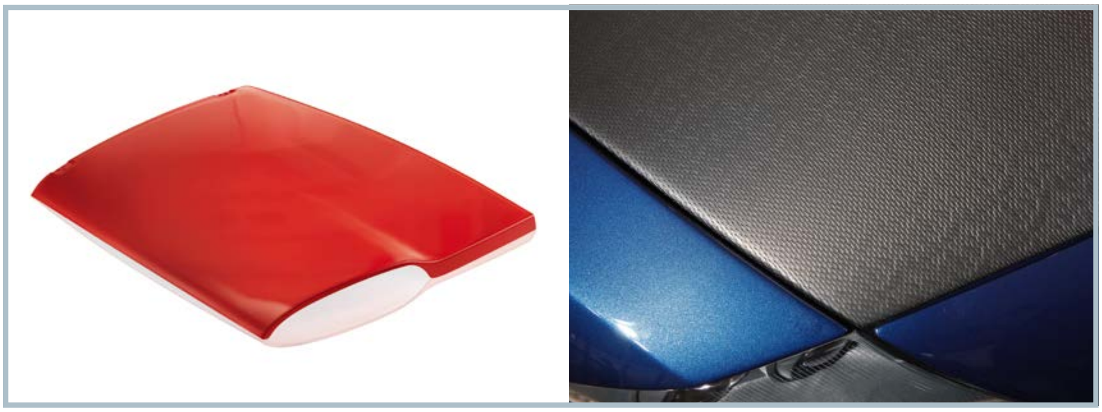

Fig. 6. Left: CFRP roof segment of the Roding Roadster with polyurethane matrix resin: High-quality varnish thanks to injected filler varnishing; right: hood of the BMW Z4 Street Shark: The bionic surface was copied from sharks (figures: Henkel, Frimo Group)

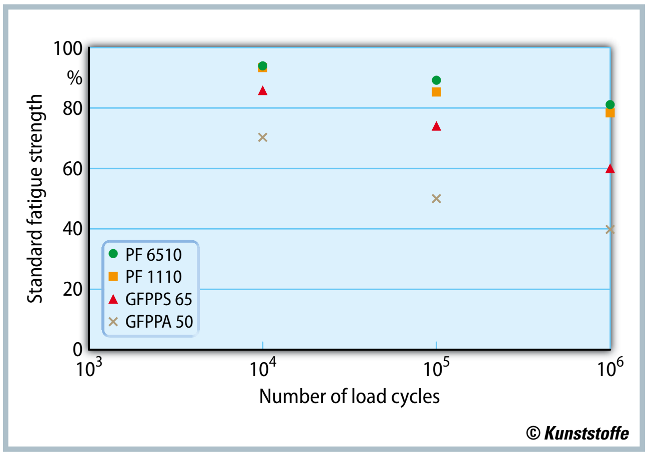

Fig. 7. The fatigue strength of phenolic resin compounds is considerably higher than that of glass fiber-reinforced high-performance thermoplastics. Tensile fatigue test, R= 0.1; 5 Hz (figure: Momentive)

Detailed reproduction of a shark skin reduces the air resistance of moving fiber composite parts significantly. This can be found in the hood and roof module of the BMW Z4 with the name "Street Shark" presented in **Figure 6, right** [18]. As part of the Vitrox group of materials, the new polyurethane raw material of Huntsman GmbH in Deggendorf, Germany, even enables a glass transition temperature above 280 °C, for special types. Such molding materials can be submitted to in-line cataphoresis varnishing, for example.

The BMW i3 also features PU composites. The CFRP rear seat shells are 1.4 mm thin, crash-resistant, and made of BASF's Elastolit material. Cupholder fixtures and storage trays are integral parts of the shells [12, 19].

From Liquid to Polyamide

Today, reactive processing can also generate high-performance fiber-reinforced plastics parts from polyamide (PA). This material features the highest strength of all reactive matrices, plus outstanding stiffness. The pellet components of BASF are composed of a basic monomer, Caprolactam, and an activator or catalyst. They are melted at temperatures above 70 °C and mixed. With a viscosity similar to water, the material is then injected into the mold, which contains a reinforcing textile fiber. The material finally undergoes anionic polymerization at approx. 150 °C, which converts it into PA6 within minutes [12].

Under high pressure, first parts for a vehicle are manufactured in the RTM process, such as a prototype of a B pillar. Moreover, a kayak was produced, too, showing that in-situ PA is also suited for the vacuum infusion technique (**Title figure**). It only took 60 s to fill the 2.60 m boat at a vacuum of 0.9 bars.

Bound to Fibers

With the new reactive systems, attention must be paid to fiber bonding, as well. In the course of the polymerization, the glass fiber size developed for reactive PA6 forms a covalent bond between glass surface and the caprolactam molecules [20]. Glass and carbon fibers applied for in-situ acrylate were also equipped with tailored sizes [11].

To safeguard the dimensional stability of the piles of fiber layers during resin injection, it is recommended to apply a curable binder spray and then treat it with heat [14]. Applying the "part-via-preform" process, a binder was previously applied to the carbon fibers that allows flexible design of long and continuous fiber prepregs [21].

Thermoset Molding Compounds

Phenolic resin molding compounds are improving their position as a thermally stable material for automotive components. In various applications of recent years, the technique of aluminum die-casting, which is more demanding in terms of process engineering, could thus be avoided. In addition to component weight, this also saves production costs. For vacuum pumps, for example, mineral and glass fiber filled phenolic resin compounds are used. Supplied by Momentive Performance Materials GmbH in Leverkusen, Germany, they feature a thermal coefficient of expansion almost as low as that of steel. What is more, the material behaves isotropically, in this respect, which is unusual with injection molded plastics. Components under the bonnet have to absorb dynamic forces resulting from the engine as well as traveling, which is why fatigue strength is a major aspect. After 10^6 load cycles, the fatigue strength of phenolic resin compounds is reduced by only 20 %, roughly (**Fig. 7**) [14].

Conclusion

A step has been taken towards automated processing of reactive composites, while innovative liquid systems are available for all types of applications. From an engineering point of view, the outlook could hardly be better for the fiber composite industry. ■