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Creating GRP Tools Quickly and Economically Using Nanotechnology

A new tooling system by Büfa offers high-quality mold surfaces and superior efficiency. In focus: an improved curing chemistry that allows the manufacture of especially thick laminates comprising of thin layers as well as a gelcoat that can effectively discharge static electricity via carbon nanotubes.

Setting the Course for Surface Quality

Unsaturated polyester resins are still the material of choice when it comes to the manufacture of premium and aesthetically pleasing Glass Fiber Reinforced Plastic (GRP) parts in small to medium-sized series, for example those used in producing cars, boats, rail and commercial vehicles, tanks, pipes, swimming pools and sanitary facilities. In this regard, mold tools (which serve as negative molds for making actual GRP products) are subject to especially high requirements. Their surface quality is crucial for the look and feel of parts made in them. If something is neglected here, it will take a lot of effort to iron out the problem in later parts of the manufacturing process. This means everything must be highly glossy and free of defects from the very beginning.

However, there has hardly been any relevant advancement in the field of mold tooling systems in recent times. In comparison, polymer chemistry has progressed greatly in the past years; for example, modern tooling resins have been optimized in terms of their shrinkage behavior thanks to a thermoplastic phase. Based in Rastede (Germany), Büfa Composite Systems is a supplier of customized special reaction resins and all-in-one solutions for the production of GRP parts. The company is now introducing a new, innovative tooling system that incorporates some of these advancements – the result is a new tooling system that combines increased efficiency with further improved surface quality. Likewise, this new development pushes current process-related limits and can be processed using conventional methods despite their high-performance chemistry.

Electrostatic Charges Hinder Work

The gloss level is important for assessing the surface quality of molded parts made of glass fiber-reinforced, unsaturated polyester resins, Figure 1; the key here is Class

Single-walled carbon nanotubes act like tiny strands of wire in the reaction resin's matrix on a submicroscopic level.

and offers new levels of freedom, for example in terms of the minimum/maximum thickness and number of resin layers that can be applied in each work step. Another key advantage of the new development is that the new systems remain easy to use A surfaces. In practice, the appearance of a GRP part can be significantly affected by dirt and dust accumulated on the surface of a mold tool. Conventional tooling systems are hardly able to prevent this from happening.

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This is caused by what is known as the triboelectric effect, which refers to the buildup of an electrostatic potential between two insulators (such as most types of plastics) that are moving relative to each other. Depending on the air humidity, molding surface, demolding method and even demolding angle, static electricity can build up between GRP molds and GRP parts in the order of a few dozen kilovolts, which can often result in sparks caused by static discharges.

Such static discharges are not only a source of irritation for workers but can even injure them. Furthermore, they can increase the risk of fire (such as in the presence of organic solvents) and cause severe damage to sensitive equipment. An electrostatic buildup also causes a force of attraction that makes it more difficult to release a part from its mold, which can result in damage to the material on the part or even on the mold tool itself. In the worst case, this effect can even reduce the lifespan of the mold tool.

Above all, however, electrostatically charged surfaces attract dust, which necessitates the time-consuming process of cleaning each time a part is demolded. Because even the best effort is hardly able to completely eliminate dust accumulation, electrostatic charges are one of the main reasons for GRP parts having poor quality.

Carbon Nanotubes Effectively Dissipate Static Electricity

In the past, there were attempts to alleviate this problem by introducing conductive additives, but all of them were accompanied by significant disadvantages in terms of their application. For example, gelcoat surfaces modified with conductive carbon black are difficult to process because this additive has a considerable impact on the viscosity of reaction resins. In addition, such surfaces are only available in deep black; other kinds of fillers such as graphite and carbon fibers also cause a black coloration. Another issue is that the gloss and chemical resistance of these surfaces do not meet the desired standards for tools made of reactive resin.

Büfa uses what is known as Single-walled Carbon Nanotubes (SWCNTs) in the company's new Conductive Tooling Gelcoat GC H/S. The SWCNTs do not have the same drawbacks. This special form of carbon nanotubes has a high electrical conductivity and a good length-to-diameter ratio.

In other words: SWCNTs act like tiny strands of wire in the reaction resin's matrix on a submicroscopic level. At a low concentration (percolation threshold), they start to form a network of fine, molecular "wires" that run through the material, Figure 2 and Figure 3. This is how gelcoats enhanced with SWCNTs get their high electrical conductivity. The surface resistance of the new Büfa gelcoats



FIGURE 1 Dust accumulation caused by static electricity, and shrunken surfaces can be minimized thanks to the new, antistatic tooling system consisting of an antistatic gelcoat, an optimized first-layer resin and tooling resins (© Büfa)

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FIGURE 2 Schematic diagram of SWCNTs; some types of SWCNTs possess an exceptionally high electrical conductivity (© Büfa)



FIGURE 3 Even at relatively low concentrations, SWCNTs are already able to form conductive networks in the synthetic resin matrix; this gives the resin its antistatic properties (© OCSiAI)

can be effortlessly reduced to a constant value of about 10⁶ ohms, which means they are around 1000 times more conductive than what is required of antistatic surfaces.

Reduced Cycle Times, no Electrostatic Build-up

Thanks to the gelcoat's conductivity, static electricity generated during demolding of a GRP part can be discharged very effectively using a simple earth connection. This results in easier and quicker demolding, Figure 4, shorter tool-cleaning times, decreased cycle times, reduced scrap rates, and improved part quality. It also prevents the much dreaded electric shocks, which in turn significantly reduces the risk of fire. To achieve a comparable effect using graphite or carbon black, they would have to be added in amounts ranging from 100 to 500 times of what is required for nanotubes. The conductivity of the gelcoat remains intact even after a GRP mold tool has been sanded or polished, as the SWCNT networks cannot be removed by surface abrasion. Unlike carbon black or carbon fibers, the nanotubes are invisible to the human eye thanks to their fine molecular structure. This allows the tool surface to retain its gloss even after being sanded and polished, meaning the surface quality remains practically the same after this treatment.

Furthermore, due to the low concentration of nanotubes in the gelcoat, they only have a slight impact on the gelcoat's coloration. This allows the antistatic gelcoat to be colored in many different hues using conventional pigment types. Although this property may not necessarily be of importance for toolmaking, it is absolutely crucial for other applications (such as control panels with antistatic walls).

Faster Curing and Higher Dimensional Stability

The conductive gelcoat is just one of three components of Büfa's new tooling system. In a GRP tool, underneath the visible gelcoat are two other resin systems that work together with a fiberglass mat to give the tool its required strength, Figure 5. One of them is the first-layer resin, which is used to wet and stabilize the gelcoat layer (which is merely 1000 µm thick) and therefore has a large impact on the tool's surface quality. The other is the actual tooling resin, which constitutes the bulk of the tool and determines the tool's mechanical properties. Both resins must be optimally designed for their specific purposes. Büfa has also thoroughly reworked these two tooling resins.

For the new first-layer resin Büfa Resin VE 910 – as with the gelcoat – the focus was on further improving surface quality. The new gelcoat carrier excels in terms of its minimal shrinkage during curing, good wetting properties and a good stressto-strain ratio. After fully curing at room temperature, the resin will leave a thin first layer with an extremely low residual monomer content. This minimizes the amount of post-cure crosslinking, which can neg-



FIGURE 4 Antistatic properties make for easier demolding; the required force is much lower, which has a positive impact on a tool's lifespan and on scrap rates (© Büfa)

atively affect the waviness of the tool surface. The result is a smooth Class A surface that does not tend to shrink. In a Barcol hardness test, the Büfa Resin VE 910 (cured for 24 h at 20 °C, two layers of 225 g/m² CSM) was able to achieve a value of 11 – in contrast, the other comparison samples only reached a value of 4. The resin's good curing properties combined with its improved stress-strain behavior help produce molds with highly robust surfaces.

The revised formulation also improved the thermal dimensional stability of the new first-layer resin at full cure: its midpoint glass transition temperatures (TG_{mid} of about 122 °C) clearly exceeds those of the first-layer resin that Büfa previously produced (87 °C). This makes the new resin less sensitive in high-temperature applications.

Up to Twelve Layers in a Single Work Step

The Büfa Resin VE 7100 Tooling is the third component in the new tooling system. As with the other two components, it

helps simplify and improve the efficiency of toolmaking in several ways. Thanks to highly specialized low-profile additives, the vinyl ester is able to alleviate the problem of workpiece shrinkage during the curing process. This allows users to create molds that do not shrink and have excellent thermal dimensional stability (120 °C). The workability of the resin has also been significantly improved: it is characterized by its exceptionally low viscosity, which is around 50 % lower than that of competing materials. The improved flowability goes hand in hand with excellent fiber-wetting and degassing properties.

The resin's exceptional curing properties deserve special mention: its heat generation response is tailored for the production of both extremely thin- and thick-walled laminated structures. As with other vinyl ester resins, the curing process is initiated by adding peroxide. A special aspect of the new system is that both the open times and the curing times can be easily controlled by adjusting the peroxide concentration. This is important when making large parts, for example, where this concentration has a comparatively low impact on the curing temperature (T_{max}) . This is not only advantageous in terms of improved process reliability but crucially also allows users to produce laminates with up to twelve layers in one single work step (T_{max} for 12×450 g/ m² CSM: 54 °C).

This is a level of performance that is yet unseen even in high-end tooling systems by Büfa. It not only allows work to be performed more quickly, but also signifi-



FIGURE 5 GRP parts made of unsaturated vinyl esters usually consist of several layers that are formed by specially designed resins; the surface quality is in part determined by the first-layer resin (© Büfa)



FIGURE 6 An earth connection point every 7.5 m is enough to discharge static electricity even from large tools (© Büfa)

cantly increases the efficiency in tool production. Until now, when making thicker GRP laminates, only around five layers could be applied in one intermediate step. Then the layers had to be fully cured before crucial anti-shrinkage reaction is already initiated at as low as 30 to 31 °C, allowing users to create double-layer laminates with a thickness of about 2 mm that can be reliably cured and replicated. In conventional

The conductivity of the gelcoat remains intact even after a GRP mold tool has been sanded or polished.

subsequent layers could be applied. Now users no longer have to wait for the layers to cure between intermediate steps; for larger projects, this can mean reducing the overall production time by days.

Accessibility of Laminates with Extra-thin Walls

On the other end of the spectrum, the new Büfa Tooling Resin is also excellent for extra-thin laminates. Thanks to the Tooling Resin's well-balanced chemistry, the tooling resin systems, at least around four to five layers are required to achieve the heat necessary for kick-starting this reaction (around 35 °C).

Thin-walled products made by using the Büfa Tooling Resin are top-notch in terms of their performance: when fully cured, they can achieve a Barcol hardness of up to 55; tempered workpieces can even exceed this level of performance. Such thin-walled laminates also have exceptional thermal dimensional stability (75A HDT, 104 °C).



FIGURE 7 The components of the new Büfa mold-tooling system can be applied using conventional methods such as the spray-up process (example: gelcoat, left) and hand lay-up process (example: first-layer resin, right) (© Büfa)

This allows significant material savings and helps to manufacture products that are otherwise not economical to produce. Moreover, the resins offers a greater level of freedom when making highly complex parts with complicated geometries, such as thick laminated structures. The tooling resin's "mild" chemical composition also conveniently helps extend its storage life; on top of that, its exceptionally low Volatile Organic Compounds (VOC) content (< 30 %) contributes to ensuring occupational safety.

In Practice

The new tooling resin (as with the firstlayer resin) is suitable for both the hand lay-up and the spray-up methods. Like the other components in the new system, the product is easy to use and does not require users to switch to other application methods.

Essentially, the new Büfa gelcoat can be applied in the same manner as on a regular GRP part. For tools of ordinary sizes, just one single metal conductor or earth connection point, Figure 6, installed on the fully cured resin after applying the gelcoat (hand lay-up or spray-up methods, Figure 7, left and right), is enough to effectively discharge static electricity. Measurements taken by TÜV Nord in mid-2018 have shown that the antistatic properties of the SWCNT gelcoat even fulfil the stringent requirements for use in Ex Zones 2, 1 and 0 (the highest hazardous area classifications). For large-scale parts, an earth connection point should be installed every 7.5 m. The user is free to choose where to place each point.

Release agents such as Büfa BF 700 Mould Release Wax Paste (carnauba wax) can be used without any issues. Although they can very slightly decrease the gelcoat's surface conductivity, this reduction is insignificant in practice. In fact, the release film can even benefit from the gelcoat's lower tendency to attract dust. The SWCNT gelcoat also does not require any changes to be made in terms of logistics and storage; its storage life is comparable to that of conventional tooling systems.

Conclusion

The new antistatic tooling system of Büfa solves a whole host of problems often faced by users when they are working with unsaturated polyester resins to make high-quality GRP parts. The innovative, antistatic gelcoat features some of the most obvious benefits: it improves the surface quality of polyester resin parts because tools made with the gelcoat practically do not attract any dust (which may leave impressions on the finished product). In addition, the reduced effort required for cleaning helps decrease the cycle time and allows a mold to be reused within a shorter period. A tool will also have a longer lifespan because it is subject to lower mechanical stresses during

demolding. This means the new gelcoat improves both the quality of molded parts and the process efficiency.

Despite these advantages, Büfa's new tooling systems do not require any changes to the usual application processes: the systems can be applied using the same methods (hand lay-up or spray-up) and tools as those used for applying conventional gelcoats.

Environmental considerations have become increasingly important for the end customers in the past years and naturally should not be overlooked in this closing section. The low VOC content of the new Büfa Rapid Tooling Resin makes as good a case for reactive resin as it increases process reliability and reduces material consumption, which helps to reduce waste and hence costs. Even the reduction in force required for demolding contributes to the sustainability of the process by helping to reduce scrap rates.

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