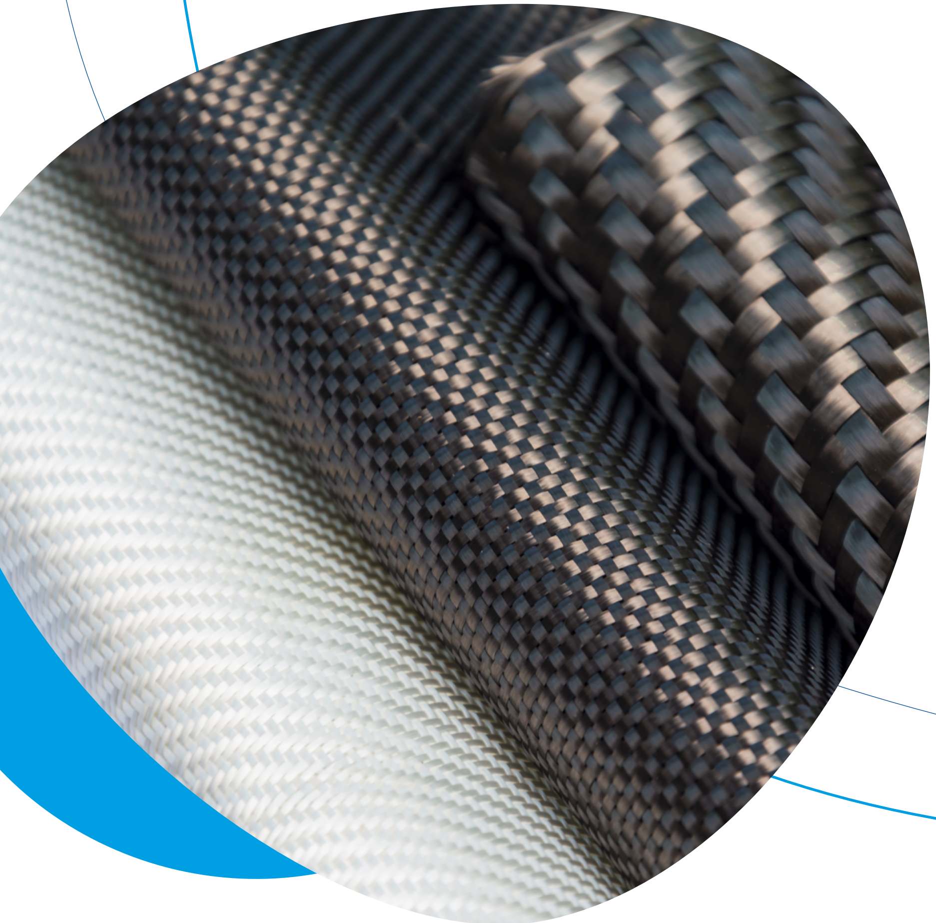

APPLICATION INFORMATION

COUPLING AGENTS: STRENGTHENING THE WEAKEST LINK IN THE COMPOSITES CHAIN

TS-A 12

A member of ALTANA

Contents

Introduction

The increasing importance of wind energy and electromobility inevitably results in a greater need for lightweight solutions that simultaneously guarantee high mechanical stability and reliability. Coupling agents build a strong bridge between resin and reinforcement, enabling more durable and long-lasting materials while increasing design freedom.

For additional information on additives and technical topics, please contact us:
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Note

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Performance-limiting interfaces

Composites based on thermoset materials have become an essential part of our daily life. They find application in established goods such as sanitary ware or sporting equipment. Moreover, they are also accompanying technology changes by giving access to crucial components, for example in wind turbines and electric vehicles.

In many cases, composite materials are comprised of a combination of a cross-linked organic polymer (matrix) and inorganic materials, such as particulate fillers or fibers. While the inorganic material can also have the function of a cost-effective filler, it often improves surface quality, flame retardancy, or abrasion resistance of the final composite. Fibrous materials (such as glass fibers or carbon fibers) help to significantly enhance the mechanical properties of the composite, such as tensile, flexural, and shear strength, while contributing to a lower weight of the final part compared to non-composite materials. Without this inorganic reinforcement, lightweight materials required for reduced emissions, fuel efficiency, and renewable energy would not be possible.

Despite the beneficial nature of the inorganic components in the composite, the boundary between the matrix (resin) and the inorganic part may turn out to be the weakest link of the overall system, limiting its maximum performance. With respect to this boundary effect, though it may be possible to improve single components, such as resins, fillers, or fibers, there is a certain limit to the possible optimization of each individual component. Taking into consideration the relevance of the organic/inorganic boundary, an improved link between the resin matrix and the dispersed phase (fillers, fibers) can result in improved mechanical properties. An easy way to achieve the desired coupling are additives that have the ability to cross-link with the resin and form a bond to the filler or fiber. These additives are known as coupling agents.

General structure and working mechanism of coupling agents

Coupling agents provide a connecting function between the organic resin matrix and particulate filler or fiber materials by establishing strong bonds to the surface of the filler/fiber and cross-linking into the matrix during the thermoset curing process. This strong connection between the organic and the inorganic components of the formulation results in increased mechanical properties of the composite material prepared. To become efficient, the coupling agent needs to be employed in a system where the weakest boundary of the composite is the interface between filler/fiber and resin (G. 01). This means a coupling agent cannot prove value if the material failure is caused by cohesive fracture of the resin or the inorganic component.

In general, a coupling agent contains at least two types of functional groups:

(1) a reactive group which is able to copolymerize with the matrix during the curing process, and
(2) a highly affinic group which is able to adhere strongly to the surface of the particle or the fiber.

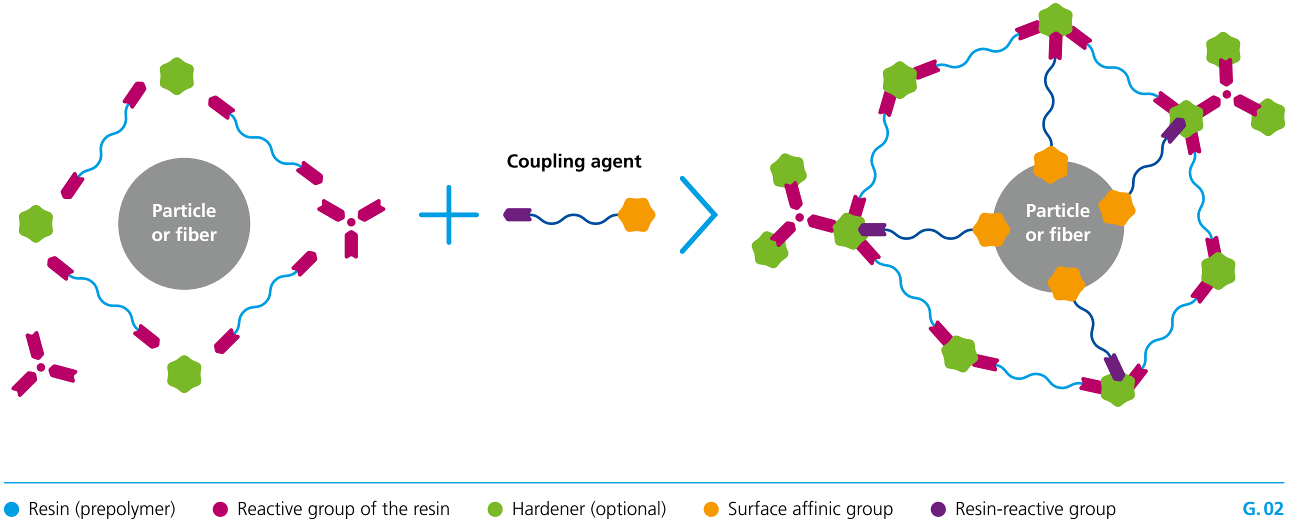
For example, in a free-radical curing system (such as an unsaturated polyester or acrylate system), the coupling agent likely comprises polymerizable double bonds. If the thermoset system is cured via a two-component mechanism (2-pack system, such as most epoxy or polyurethane systems), the coupling agent may be reactive towards the resin or the hardener.

The general mode of action is shown in G. 02, in which the composite system is shown before curing and after curing is completed. Surface affinic groups of the coupling agent adhere to the surface of the inorganic component(s) used. At the same time, the additive has cross-linked into the matrix. Since the coupling agent works as a bridge builder between matrix and dispersed phase, it is apparent that this additive must be designed for a certain combination of matrix and inorganic phase: **There is no universal coupling agent that will provide benefit for all combinations.**

General working principle of a coupling agent in a composite material

G. 01

Working mechanism of a coupling agent in a thermoset system



G. 02

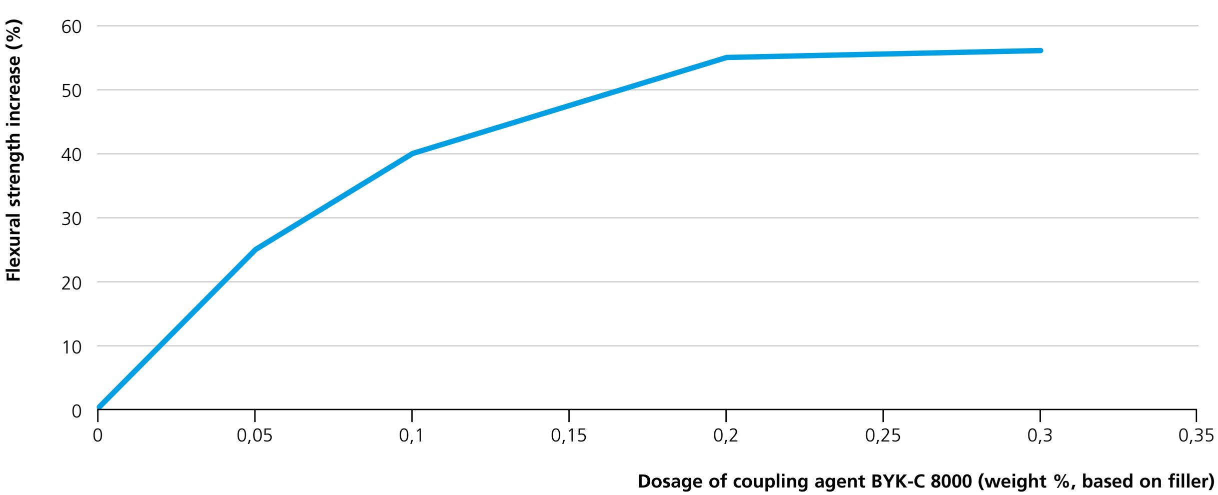
Quartz-filled unsaturated polyester system as an example for a casting application

Typical applications for quartz-filled unsaturated polyester systems include polymer concrete, artificial marble, and engineered stone. In these systems, it is desirable to increase the mechanical performance for a given part or to reduce the thickness of the construction part while having the same level of mechanical properties (material savings, cost reduction). Both can be achieved by using a coupling agent. As can be seen in G. 03, the flexural strength can significantly be increased using a dosage as low as 0.2 wt.% (based on filler). Once the ideal amount of connecting points has been promoted by the coupling agent, a further increase of its dosage cannot result in higher mechanical properties.

This effect can also be visualized via microscopic imaging (G. 04): In the presence of the coupling agent, cavities are minimized, and resin and filler are connected to each other in a robust manner.

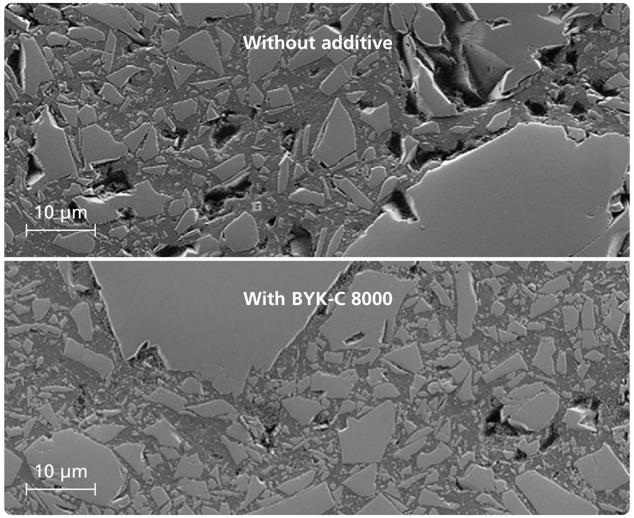
In addition to mechanical improvement, the systems enhanced with the coupling agent can provide additional benefits beyond increase of mechanical properties. Such additional improvements can comprise increased hot water and chemical resistance. This prolongs the lifetime of a construction part and minimizes the formation of blisters when exposed to humidity and temperature.

Relative improvement of the flexural strength in a quartz-filled unsaturated polyester system as a function of the dosage level of the coupling agent



G. 03

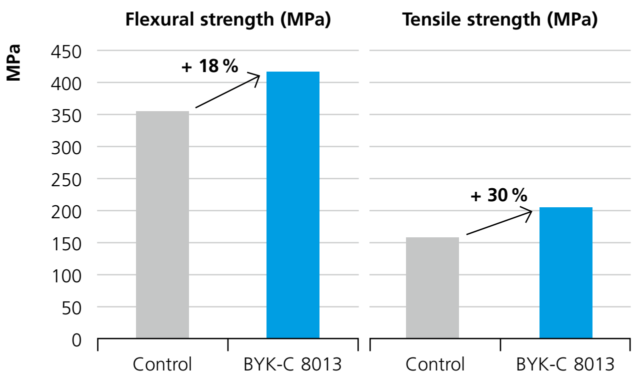
Electron microscopic image of a quartz-filled unsaturated polyester resin after exposure to hot water in the absence and presence of BYK-C 8000 coupling agent



G. 04

Carbon fiber reinforced vinyl ester system as an example for closed mold applications

Improvement of mechanical properties in a chopped carbon fiber reinforced vinyl ester system



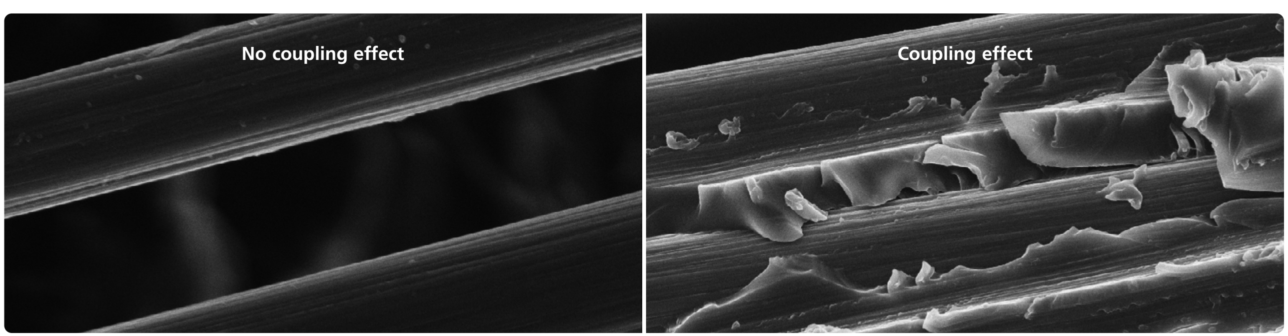
G. 05

Carbon fiber reinforced plastics are used when the need for high material strength meets the demand for lightweight properties of the composite parts. Examples for these applications comprise aerospace and general automotive industry, electromobility, and wind energy applications. In these industries, composite production is frequently carried out using, for example, RTM processes, prepregs, pultrusion, or SMC technology in combination with various resin matrix systems.

Appropriate coupling agents can provide benefits for flexural and tensile strength both for chopped fibers and fabrics (G. 05).

In analogy to the particulate filler, the mechanical improvement of the fiber reinforced system was visualized by electron microscopy (G. 06): In the absence of a coupling agent, only a few resin leftovers can be detected on the fiber surface after material failure; this clearly underlines a poor adhesion between fiber and matrix. In contrast, in the presence of a suitable coupling agent, significant amounts of resin residues can be seen on the fiber surface. In some cases, when using the coupling agent, the adhesion between carbon fiber and matrix is so strong that a fiber fracture occurs (G. 07).

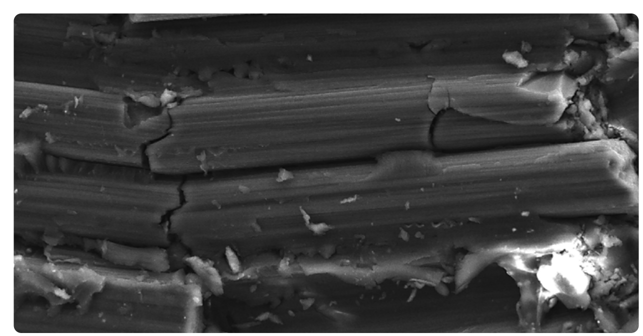
The coupling effect



Adhesive failure **Cohesive failure in the matrix**

G. 06

Electron microscopic image of a material failure resulting in a fiber fracture instead of an adhesive fracture



G. 07

Glass fiber reinforced epoxy as an example for ambient cure applications

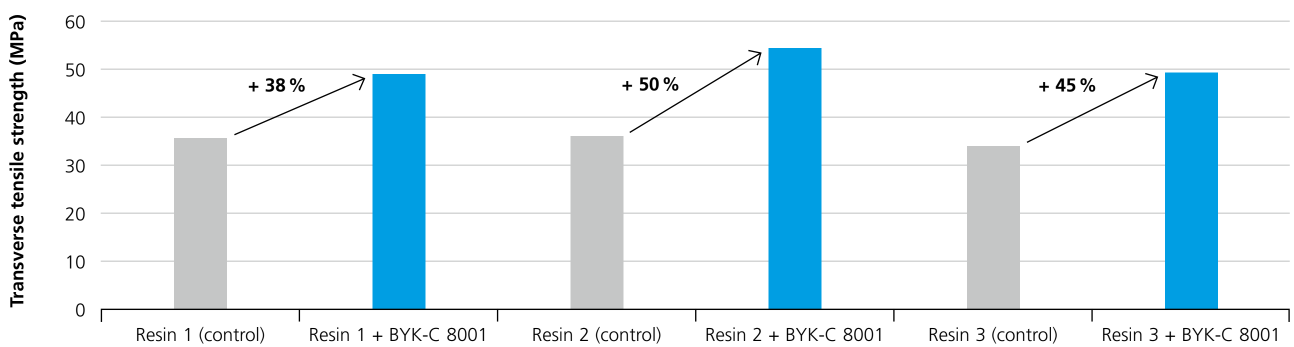
Mechanical properties of composites are generally improved by application of fibers. The most commonly used fibrous material to reinforce composites are glass fibers. Examples for such glass fiber reinforced systems can be found in wind energy, marine, sports and leisure, sanitary, construction, and building parts. As shown for carbon fiber reinforced materials, the transverse tensile strength can be significantly improved by the addition of an appropriate coupling agent. Mechanical improvements found in different resin systems are shown in G. 08.

The addition of a coupling agent can also result in improved fatigue properties. The final part is more reliable and has a longer life span. Coupling agents therefore not only improve the performance of the overall system but contribute significantly to its sustainability.

As an additional effect to the general improvement, glass fiber sizings deteriorate with age, leading to an inferior performance of the final system. Again, the coupling agent can assist to compensate this aging process, yielding composites with similar properties such as those based on virgin fiber material. This effect helps to improve process robustness for the composite manufacturer thanks to higher reliability and lower batch variations of the mechanical properties of the finished part as well as the final construction (G. 09).

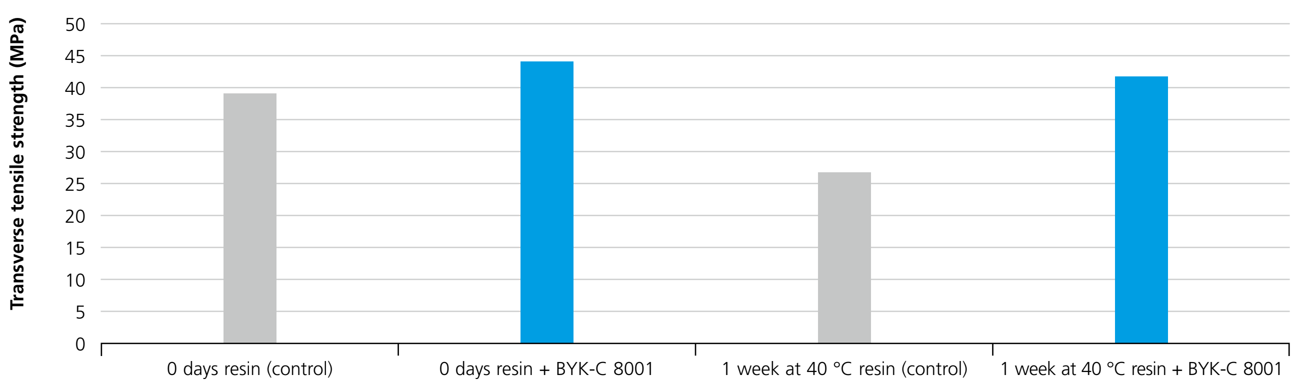
RENEWABLES CERTIFICATION
DNV·GL
Type Approval
Additive for Epoxy Resin
TA-DNVGL-CP-0089-07147

Increase of transverse tensile strength in various glass fiber reinforced epoxy composites



G. 08

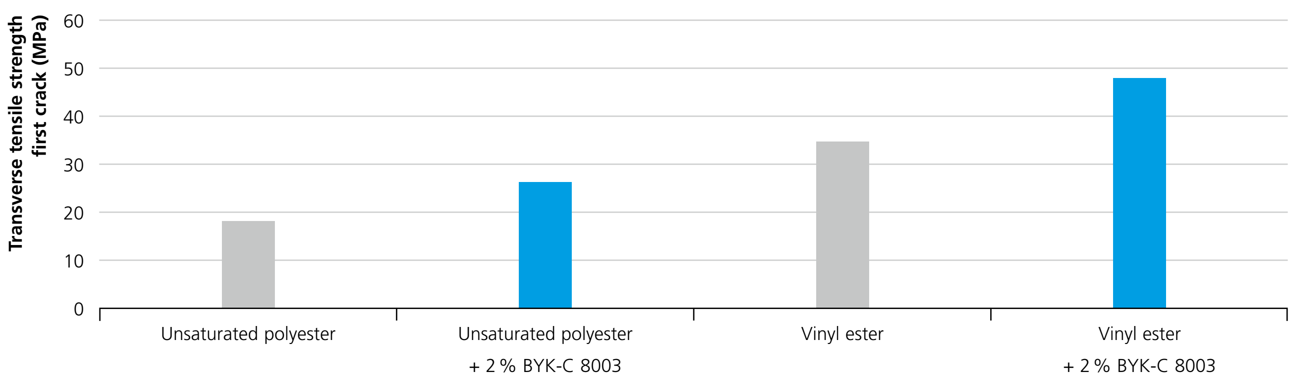
Transverse tensile strength of a glass fiber reinforced epoxy resin before and after aging at elevated temperature



G. 09

Coupling agents can also improve the mechanical properties of radically cured systems. The incorporation of coupling agents allows the system to be adjusted according to the performance requirements, even if they exceed the typical properties of the material (G. 10). Material properties of standard UP systems are shifted towards the performance of VE systems. The mechanical properties of VE systems can be further optimized.

Transverse tensile strength of various radically cured systems in presence and absence of a coupling agent



G. 10

Overview of suitable product combinations

There is a multitude of resin systems with different curing mechanisms and characteristics. Most of these can be combined with various fillers and/or fibers. This results in a vast number of material compositions and therefore in numerous possible boundary combinations. To ensure a good bonding link for all these reinforcement/matrix combinations, a variety of coupling agents represents the toolbox. The following table summarizes suitable coupling agents, which can be employed in different systems to provide improved mechanical properties and reduced quality fluctuation.

Recommended coupling agents for different combinations of resins and reinforcements

Mechanism	Resin systems	SiO_2	ATH	Glass fiber	Carbon fiber
Radical curing	UP, VE	**BYK-C 8000**		**BYK-C 8003**	For MgO thickened systems: **BYK-C 8013** For isocyanate thickened systems: **BYK-C 8014**
	Acrylate	**BYK-C 8000**	**BYK-C 8002**	**BYK-C 8003**	**BYK-C 8013**
Polyaddition	Epoxy	**BYK-C 8001***		**BYK-C 8001***	

*BYK-C 8001 is certified according to DNV-GL TA-DNVGL-CP-0089-07147.

T. 01

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Additive for Epoxy Resin
TA-DNVGL-CP-0089-07147

Conclusion

A key task for composite manufacturers is the optimization of mechanical properties. This is often achieved by the enhancement of individual components. Despite the option to improve single materials, such as resins, fillers, or fibers, there is a certain limit with respect to the influence of every specific component on the performance of the final composite part. In an alternative approach, the link between the resin matrix and a dispersed phase providing reinforcement (fillers, fibers) can be optimized. An easy way to achieve the desired performance increase is the use of additives which have the ability to cross-link with the resin and form a bond to the filler or fiber at the same time. These additives are known as coupling agents; their structure needs to be selected according to the chemistry of the matrix and dispersed phase. The coupling agents of the BYK-C 8000 family solve this task by creating a strong bridge between resin and reinforcement, giving access to more durable and long-lasting materials and allowing higher freedom of design.

Coupling agents must be tailored for a certain matrix/reinforcement combination by the adjustment of functional groups. Their improving properties can be essential to boost cost/performance levels of certain application systems. Therefore, the use of coupling agents provides access to both innovative technical solutions and cost advantages as well.

Coupling agents can be used in a large variety of systems, among those epoxy resins, unsaturated polyester resins, vinyl ester resins, and acrylate resins in combination with different kinds of inorganic reinforcements, such as quartz, aluminium trihydroxide, glass fibers, and carbon fibers.

To cover the versatility of possible matrix/reinforcement combinations, a variety of coupling agents is available. Among those, the first coupling agent has recently been qualified according to the Germanisher Lloyd certification (DNV GL); this allows end users to make use of the coupling agent without affecting existing certifications.

A multitude of material properties have been demonstrated to be improved using coupling agents. In general, tensile strength, flexural strength, elongation at break, and fatigue are in focus.

Coupling agents can be used at different stages in the process, such as (i) during the production of reinforcements (surface treatment of fillers and fibers), (ii) a part of the resin formulation (resin additive use), and (iii) upon composite production (e.g. as second sizing or directly before or during application). They can therefore be employed by all members of the value chain to differentiate from the state of the art, including manufacturers of fillers and fibers, resin houses, and composite producers.

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