Epoxy Based Matrix Systems and Adhesives for Future Rotor Blade Application

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Abstract

For liquid resin systems, a comparison of specific static and fatigue properties is drawn between epoxy (EP) and vinyl ester (VE) matrices. By the example of a 40 m rotor blade it could be demonstrated that under consideration of the better transverse strength of an UD-laminate in EP compared to VE, the rotor blade mass for the latter would have to be nearly 8 % higher to have the same out-of-plane deflection at extreme load. A lifetime estimation on the basis of measured S-N curves revealed a more than 60 times higher damage rate for a VE- than for an EP-blade.

Bonding pastes are the second EP-based system which is essential for the rotor blades. Important features such as curing temperature, glass transition temperature, curing behaviour and exothermic reactions as well as shrinkage and rheological behaviour are explained in more detail.

Introduction

Although the wind turbine development tends to larger sizes especially for offshore operation, many rotor blades still are and will be designed in glass fibre reinforced plastic (GFRP). The matrix systems commonly used in those blades are thermosets. In the beginning phase of this technology it was unsaturated polyester (UP) which was taken for the development of the blades which were relatively small at that time. However, with the increase of the rotor size of the wind energy converters, the epoxy (EP) systems became widely accepted although they are more expensive.

This may have several reasons. UP needs a certain percentage of styrene to lower the initial resin viscosity and to increase the reactivity. But with an increase of the volatiles, also the shrinkage increases (5 – 8 %). Since the shrinkage takes place in a more solid phase of the conversion, a composite will – together with a high exotherm – suffer from relatively high internal stresses. These can lead to a decrease of the strength and also the fatigue qualities. Another disadvantage is the relatively high energy input for the suction to keep within the maximum allowable concentration (MAC) when no RTM-method is applied.

EP on the other hand offers shrinkage of only 2 – 5 %, the internal stresses in laminates are lower compared to UP and they have outstanding adhesion to the fibres, leading to excellent static properties like e.g. strain at break or – in a laminate – interlaminar shear strength (ILSS). Beyond

UD-GFRP	Epoxy	Vinyl Ester
R_{1Z}, MPa (0°)	920	722
R_{2Z}, MPa (90°)	72	64

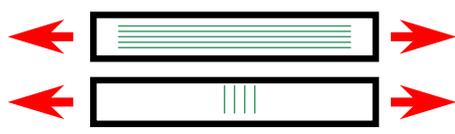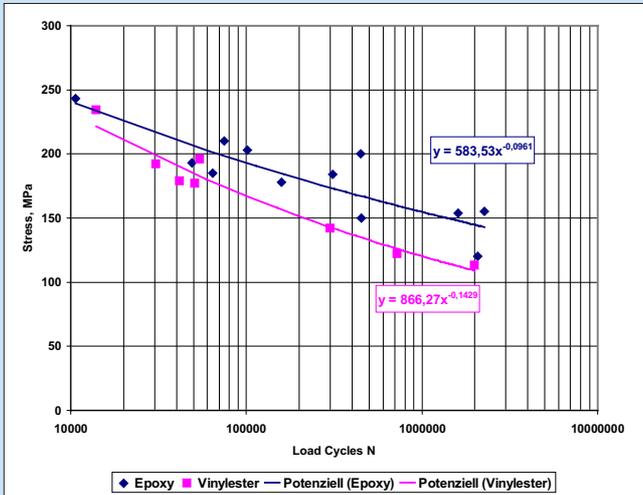Tab. 1: Static properties of EP- and VE-laminates in 0°- and 90°-direction

Fig. 1: S-N curves of Triax/UD-laminates, Risø-measurement
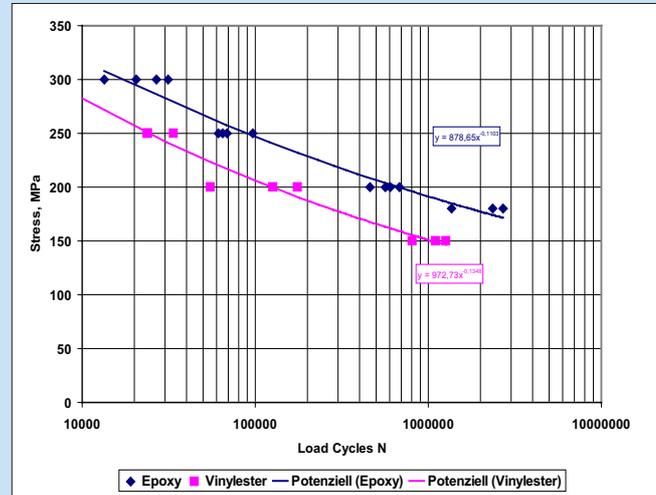
Fig. 2: S-N curves of Triax/UD-laminates, Hexion-measurement

	Exponent	Slope
EP-Laminate / Risø	-0,0961	10,41
EP-Laminate / Hexion	-0,1103	9,07
VE-Laminate / Risø	-0,1429	7,00
VE-Laminate / Hexion	-0,1348	7,42

Tab. 2: Slopes of measured S-N curves for EP and VE-laminates

that, the fatigue properties of EP laminates expressed by the slope of the S-N curve are admittedly better than those of UP laminates.

Nowadays, UP seems to become more interesting again for blade manufacturers. But also vinyl ester (VE) resins are in discussion. They are chemically and mechanically between UP and EP. Additionally, they are cheaper than EP and good to handle. The paper will highlight some static as well fatigue properties of VE and compare them with EP.

Beside the liquid matrix systems themselves also the adhesives play a big role in a rotor blade and follow highly challenging requirements. An adhesive has to fulfil several important functions. It must bond together the leading and the trailing edge as well as the spar onto the shell. Thereby, it often must build a bridge over a gap of up to 30 mm. This implies that it should have low shrinkage to withstand the induced multidimensional stress state. Technologically, it should offer excellent handling qualities. Tight cycle times for action periods of the moulds, good fracture toughness and also a similar high glass transition point as the laminate resin are additional demands for a bonding paste. EP-based glues are an outstanding means to fulfil those requirements and to ease the certification process.

Thus, in the second section of the paper, the requirements on bonding pastes are presented elaborately. The examples for the EP resins and bonding pastes are based on the experience with and measurements on systems produced at Hexion.

Liquid Epoxy Resins

In this first part of the paper, some major static and fatigue properties of liquid EP and VE resins systems are compared and examined with respect to their effect on the mass of a typical GFRP-rotor blade of a length of 40 m. For this case a stress analysis was carried out by the company Aero Dynamik Consult (ADC) according to the requirements of the GL, Edition 2003 [1]. For the special case, fibre fracture and inter-fibre fracture exertion as well as damage accumulation were calculated for extreme and fatigue loads. For this pre-design, the properties of UD-, Biax- and Triax-laminates were used.

For the EP-system, the Hexion-product MGSRIMR135 with MGSRIMH1366 was selected, which is widely used in rotor blades since several years. The static properties for the EP system were measured at specimens which have been manufactured in-house. For the comparison, a typical VE

system was selected. It was decided to use the static VE-properties of UD-material for the analysis because those are published in technical information sheets of the VE-producer.

For the damage analysis, S-N curves were established. For this purpose, Triax-/UD-specimens were manufactured with MGSRIMR135/MGSRIMH1366 as well as with the same VE-matrix the static properties are published with.

<u>Consequence of static properties of an UD-laminate on the mass of a rotor blade</u>

The static properties presented in Tab. 1 were conducted from the in-house measurements with the EP-system and from literature for VE-system.

According to the GL-requirements, the transverse strength R_{zz} is a criterion for the maximum static load on a rotor blade. To avoid possible Inter Fiber Fracture (IFF), R_{zz} must not be exceeded. The stress analysis revealed that, as shown in the figure above, the EP-laminate has a higher transverse strength by seven percentage points compared to vinyl ester laminates. Considering the concrete case of the 40 m blade tip, this results in 4.63 m of deflection for a GFRP epoxy blade and in 4.99 m of deflection for a GFRP vinyl ester blade. To achieve comparable deflection between the two materials (e.g. to avoid tower collision), the VE-blade would need a 7.8 percentage points higher mass. That means in absolute figures that a 40m blade of EP would need a lower mass of around 450 kg compared with a VE-blade.

<u>Consequence of fatigue properties of an UD-laminate on the damage accumulation of a rotor blade</u>

Fatigue tests on Triax/UD-specimens were performed at the lab of Hexion and – for comparison purposes – at Risø DTU, the National Laboratory for Sustainable Energy of the University of Denmark. The specimens for both the EP and the VE-laminates were manufactured under comparable conditions by Hexion. The fatigue tests were conducted in both labs in tensile-compression loading (R=-1). The results are presented in the Fig. 1 and 2.

A characteristic feature of an S-N curve is the slope which is generated from the reciprocal value of the exponent in its equation. The exponents and slopes for the 4 resulting fatigue curves are presented in Tab. 2. There are minor differences in the figures of Risø and Hexion. But these refer to the common scatter in material and specimen quality rather than to testing differences of the laboratories. Obviously, there is no trend that one lab would produce the better or worse slopes of one respective material combination.

It is clearly visible from these figures that the VE-fatigue curves have a much steeper course than EP. Thus, a quite shorter lifetime of a VE rotor blade can be expected compared with an EP blade. For this purpose, a damage calculation was carried out by ADC for a 20 years lifetime of the anticipated 40 m rotor blade with the two matrix systems. The calculation was performed according to the GL-require-ments in [1]. In this simulation, the more favourable slope of 7.42 was assumed for VE, and the worse slope of 9.07 for EP. The maximum strain in the spar cap of the blade for this comparison was 166 MPa.

As a result it was shown that – by the application of the linear Palmgren-Miner rule – the damage accumulation factors were around 0.1 in flap- and edgewise direction for EP and more than 6 for VE. This high ratio of damages between a VE- and an EP-blade was also found by means of a lifetime estimation carried out redundantly with a DLR program using the WISPER standard [2-4].

As a consequence of the relatively high damage rate on the fictive VE-blade it was stated that the stress/strain level of a VE-blade at the areas concerned would have to be lowered for about 28 % to achieve a damage accumulation factor <1. To achieve the same damage the epoxy matrix can take, the stress/strain level had to be lowered by even 58 %.

It should be mentioned that the sizing on the fibres plays a dominant role for the adhesion between fibre and matrix. The sizing on the glass fibres is normally universally applicable for UP as well as for EP and also for VE resins. Thus, the evaluations and conclusions from the comparisons between the composite properties of the various resin systems are drawn on a fair basis.

Epoxy Bonding Pastes

<u>Cure temperature (T_{cure})</u>

The cure temperature may limit the glass transition temperature of a curing epoxy formulation. This is a problem if the cure temperature lies below the maximum attainable glass transition temperature ($T_{G,ult}$). As a result of insufficient cure temperature or cure time, the glass transition temperature (TG) may remain below its potential ($T_{G,ult}$). In general, the performance of the resulting partially cured material also remains below its potential.

The maximum attainable glass transition temperature ($T_{G,ult}$) is a material property that depends on the selected components in the epoxy system. The maximum available cure temperature (T_{cure}) therefore restricts the design of the epoxy system - if partial cure and substandard performance are to be avoided.

<u>Curing behaviour and exothermic reaction</u>

All epoxy systems produce heat during the curing reaction: the reaction is "exothermic". This heat raises the temperature of the formulation during the cure. As a result, the true cure temperature in an epoxy system lies above the applied oven or mould temperature.

The extent to which the heat can raise the temperature above the cure temperature depends on

- the heat capacity of the formulation itself and
- the heat exchange with the environment (volume/surface-reaction).

The reaction heat and heat capacity are material properties that depend on the selected components in the formulation. The heat exchange depends on

Fig. 3: Different rotating viscometer types for measuring the rheological behaviour
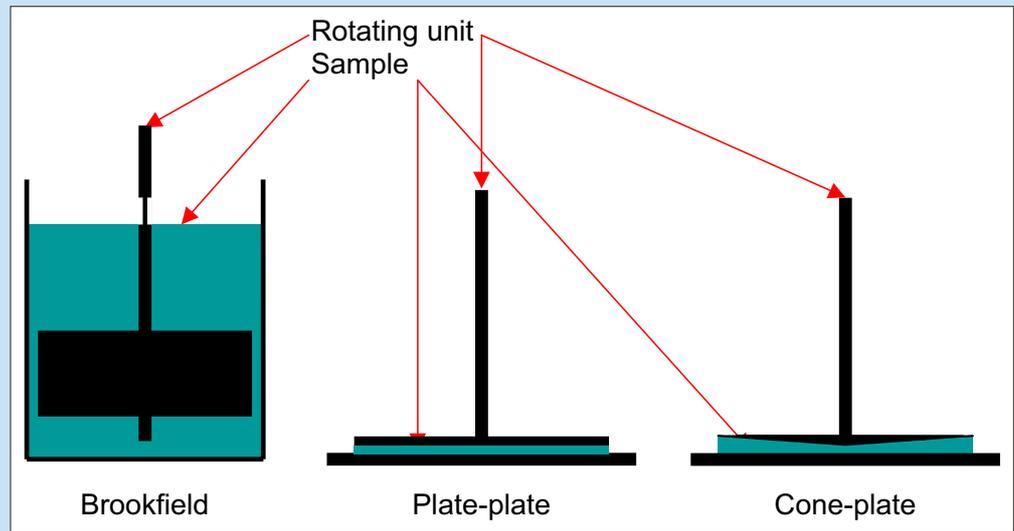
material properties of the formulation (e.g., the heat conductivity),
- material properties of the formulation (e.g., the heat conductivity),
- oven design or mould design,
- the temperature profile during the process (temperature difference formulation-environment) and
- last but not least the geometry of the part which is cured (surface/volume relation).

The exothermic temperature increase may become excessive if it exceeds the maximum temperature of secondary materials (e.g. the foam used for sandwich structures or the vacuum membrane). Ultimately it may reach the thermal decomposition temperature of the epoxy system itself.

As a result of the temperature increase, the reaction accelerates (cf. Arrhenius law). As a result, the same reaction heat is released faster. If the heat flow to the environment does not compensate enough, the temperature increases more than expected. In turn this will accelerate the reaction even more, releasing the heat even faster, and so on. This catastrophic scenario is called a "runaway" reaction. Countermeasures should be planned to avoid injuries or damage to property and the environment.

Therefore the material properties of the epoxy system should be balanced with the cure cycle to make optimal use of the exotherm and avoid overheated and over-cured material.

Shrinkage

It is often claimed that epoxy systems undergo a shrinkage of 2-3 % upon cure. This is typical value purely due to solidification (entropy related: loss of degrees of freedom). In addition there is the impact of thermal expansion (and shrinkage), and its difference between the uncured (liquid) and cured (solid) state. Whenever a shrinkage figure is given, it is necessary to also mention the measurement method and the parameters of influence:

- Measured temperature of the liquid (uncured) phase
- Curing cycle:
    - Cure cycle: temperature profile in time
    - Time and temperature at which gelation occurred
- Measured temperature of solid (cured) phase

As far as the measurement is concerned, there are mainly three possibilities to choose from:

1 Comparison: density in the liquid phase – density in the solid phase
2 Measure the shrinkage in an open container
3 Other methods

In the first method, the linear shrinkage can be calculated via the difference in density:

$$ s = \sqrt[3]{\left|1 - \frac{V_{solid}}{V_{liquid}} \cdot 100\right|} = \sqrt[3]{\left|1 - \frac{\rho_{solid}}{\rho_{liquid}} \cdot 100\right|} $$

Therefore, a density measurement of the liquid phase and one of the solid phase is required. Measuring the density of an epoxy mixture in the liquid phase works out very well for infusion or hand laminating resins, but when it comes to bonding pastes, the "liquid phase" is not really "liquid" and therefore the measurement is not as simple. One way to get results is to work with a Pyknometer, but the accuracy of this method depends heavily on the used Pyknometer, on the degassing history of the material, on the viscosity of the material and also on the person working the instrument. Therefore, gaining data for the liquid phase of bonding pastes can be a little tricky. The solid phase measurements are simple, because of ease of handling. One possibility to measure the density of a cured piece of Epoxies is the buoyancy method.

In the second method, the obtained shrinkage largely depends on the cavity the mixture is applied to. The shrinkage is then measured as the relative dimension change. However, if the formulation remains liquid during shrinkage, shrinkage only occurs along the vertical axis. The amount of shrinkage depends on relation between the horizontal cross-section and the height to which the mould

was filled. If the horizontal cross-section is not constant along the vertical axis, the shrinkage becomes complex to describe. If shrinkage continues after gelation, the cross-section of the reacting mass also changes and does no longer represent the linear shrinkage.

A brief comment on the third case: some methods can determine the shrinkage with reliable accuracy, but also have disadvantages. Firstly, the sample size often is too small for significant exothermic behaviour to appear, secondly they require transparent materials. These methods apply linearly polarized laser light in the 400-900 nm waveband or IR light and determine the molecular displacement.

Example: For the combination of MGSRIMR135 with MGSRIMH1366, the density in the liquid phase is 1.087 $^g/_{cm^3}$ at 25°C, the density in the cured solid phase is 1.15 $^g/_{cm^3}$ at 25°C after a curing cycle of 3h@65°C right after mixing. With the above-mentioned formula, the shrinkage can be calculated to be 4.5 %.

Rheology

A bonding paste should behave as a liquid while transferring and mixing it. However, once applied, it should remain in place and should therefore behave as a pasty solid. This pasty solid should remain plastically deformable long

enough to allow positioning and combining the blade halves. Later, once these are in place, it should become a solid with excellent mechanical properties. This is achieved through chemical crosslinking (cure), which should happen as fast as possible to keep the production cycle time as short as possible.

Rheology is the science that allows characterising the transition from a viscous liquid to a pasty solid. Viscosity is a material property. Although it is a function of temperature it is, in principle, independent of the measuring method.

For "well-behaved", "Newtonian liquids" simple viscosity measurements can be characterised via their kinematic viscosity, based on drag force measurements using Stokes Law (after correcting for the fluid density). Examples are "falling ball" and "rising bubble" measurements or capillary measurements with so-called "Ubbelohde" viscometers.

However, for non-Newtonian liquids like pastes, the viscosity depends on shear and shear history. This complicates the measurement and requires more sophisticated, dynamic viscosity measurements (dynamic because they allow varying the shear). Typically these are performed with rotational viscometers that allow controlling the shear, shear field and shear as a function of time. Examples of these viscometers are

- Couette-type with a rotating spindle (cf. Brookfield DVII, Haake, Stormer, Stabinger), non-uniform shear field,
- Searle-type with a fixed spindle (or bob) in rotating cylinder (cf. Fann), non-uniform shear field,
- Plate/Plate: non-uniform shear field,
- Cone & Plate: rotating cone on stationary plate: uniform shear field.

Because of the added complexity it is essential to report the method, equipment type and make, equipment parameters as well as the measuring conditions (time, temperature).

Generally, the equipment measures the energy dissipating through the sample, resulting in a difference of momentum.

This difference represents a force F. This force increases with the amount of deformation of the fluid in time and space: the shear rate. This shear rate depends on the rotation speed and the geometrical dimensions. Divided by the area A across which the shear occurs, a shear force τ can be derived:

$$\tau = \frac{F}{A}$$

The viscosity is defined as the ratio of shear force over the shear rate:

$$\eta = \frac{\tau}{\dot{\gamma}}$$

Summary

In the first part of the paper, the superior static and fatigue properties of liquid epoxy matrix systems were shown in a case study by the example of a fictive 40 m GFRP rotor blade. A comparison of decisive static properties between epoxy and vinyl ester revealed that a vinyl ester blade would have to be around 450 kg heavier than an epoxy blade not to touch the tower at the occasion of an extreme load.

In the fatigue case which was calculated on the basis of measured S-N curves, a vinyl ester blade would have an around sixty times higher damage rate than an epoxy blade. Thus, also for the achievement of a correspondingly higher lifetime, the design stress level would have to be lowered drastically.

The second part of the paper deals with important characteristics of adhesives which are crucial in rotor blades of wind turbines. Features like curing temperature and exothermic reactions as well as shrinkage problems and rheological behaviour are described in more detail.

References:

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[4] O. Krause, *Reliability of Lifetime Prediction for Composite Materials under Variable Amplitude Loading*, 17–20 October 2004, Atlanta, Georgia, USA, Proc. of the American Society for Composites – Nineteenth Technical Conference