MC4

Multi-level Circular
Process Chain for Carbon
and Glass Fibre Composites

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Process Chain for Carbon
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Deliverable D4.1: Sorting method for glass fibre parts

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1. INTRODUCTION & OBJECTIVE

According to the MC4 project approach, the circular chain for **glass fibres (GF)** is based on the reuse of the parts either by shredding them into smaller pieces (short term approach) or by reshaping the parts by heat and pressure (long term approach). The short term objective is to use cured, shredded GF particles as a core or filler in new GF parts. The long term goal is based on a new type of vitrimeric resin. It has the property that it can be formed into a new shape by applying heat and pressure. Parts made with such a resin can be reshaped at the end of their service life and processed into new parts. This avoids the need for matrix/fibre separation, which would damage the coating of the glass fibres and is also not economically feasible.

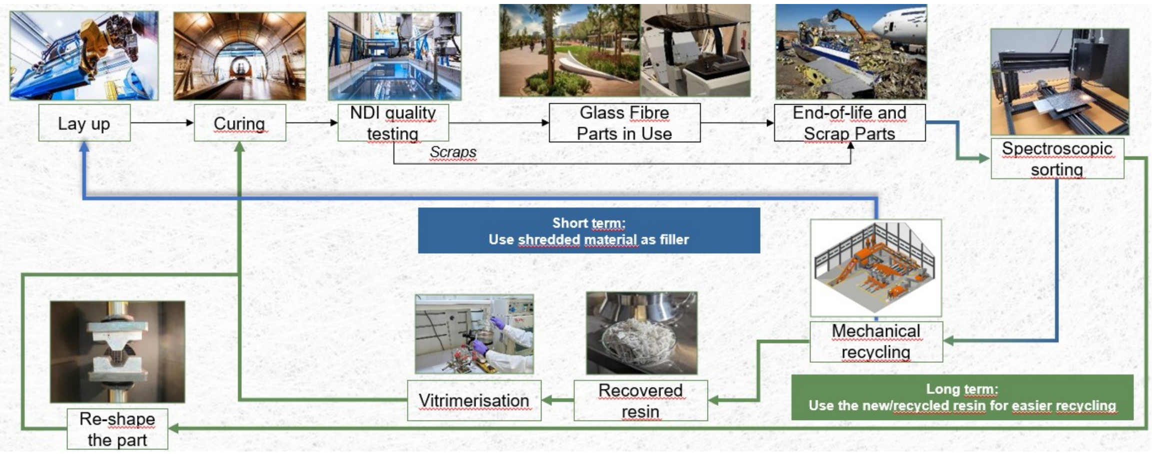

Figure 1. Circular process for glass fibre composite parts with the “short-term” and “long-term” approach.

The re-shaping process that is used for the recycling of end-of-life glass fibre composite parts requires that the parts have been made with the amine-based **3R resin** developed by CIDETEC in the project. If parts made with standard thermoset resins are used in the process, this will damage the equipment. It is thus important to **identify** parts that are suitable for re-shaping. However, resin system recognition also plays a role in the short-term approach. As the mechanical and thermal properties of glass fibre composites are significantly influenced by their resin system, there may be restrictions on the core/filler materials that can be used for certain (critical) applications. In close consultation within the project consortium, it was therefore decided to additionally search for a way to reliably identify parts made of **polyester resins**, as these materials are used in many of today's applications.

As part of this project, i-RED investigated on a laboratory scale whether methods of molecular spectroscopy, in particular **near-infrared (NIR) and Raman spectroscopy**, can be used for material detection. The study was carried out with the help of CIDETEC, VDL, Managing Composites, Lab23, and one partner from another project, who provided appropriate samples. The aim was to find the optimum method and measurement setup (reflection optics, illumination, spot size, measurement distance, etc.) for this purpose, and to assess the feasibility and possible limitations when trying to distinguish the above-mentioned resins from other types of resins commonly used for the manufacturing of glass fibre parts. In addition, an industrial concept for implementing a sensor-based solution in a mechanical sorting system (e.g., above a conveyor belt) was to be developed.

2. METHODOLOGY

2.1 Near-infrared spectroscopy

Near-infrared (NIR) spectroscopy is a technique of vibrational spectroscopy and is based on the interaction of electromagnetic radiation with molecular matter. The prerequisite for an interaction between a molecule and an electromagnetic wave is that the molecule has a *dipole moment*. Using suitable sources (thermal emitters) such as halogen lamps, specific *vibrational modes* of the molecules are excited in a sample by absorbing parts of the incident light. The light reflected or transmitted by the sample is decomposed in a spectrometer ("light analyser"). This results in a characteristic NIR spectrum that can be used to identify the types of molecules. Furthermore, it is possible to determine *multiple* chemical and physical parameters (analyte concentrations, layer thickness, pH value, degree of curing of a resin, etc.) *simultaneously* and *in real time* from a *single* spectrum.

With the NIR method, a wide range of substances (gases, liquids, solids, granular materials such as powders) can be analysed quickly and non-destructively. However, while in the so-called mid-infrared spectral regime (MIR, 3 – 50 µm) the *fundamental vibrations* of molecules are excited, in the near-infrared range (NIR, 0,78 – 3 µm) the *combination and overtone vibrations* of the molecules or functional groups are revealed. As a result, the peaks in an NIR spectrum are much broader than in the MIR spectral range and also overlap. This makes it difficult to extract information directly from the spectra. The quantitative evaluation of NIR spectra therefore requires the use of mathematical/statistical methods. This is known as *multivariate data analysis* or chemometrics. Despite the need for relatively complex data analysis, the NIR spectral range is much more important in industrial applications than the mid-infrared for physical and technical reasons. For example, in the NIR range longer optical path lengths are possible in absorbing media, inexpensive light sources and detectors (e.g. InGaAs) are available on the market, and glass can be used as an optical material (e.g. for waveguides). In addition, it is possible to employ optical switches (multiplexers) so that a single spectrometer can be used to measure at several points in an industrial plant.

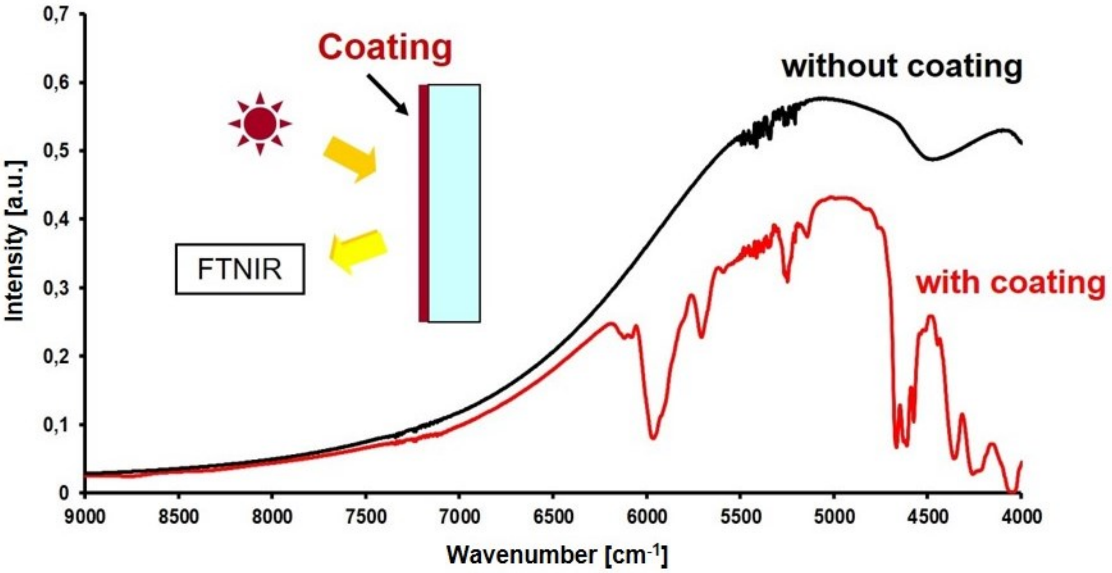

Figure 2. Principle of an NIR reflection measurement shown on a metallic sample with and without resin coating. As the pure substrate reflects the incident light freely, a spectrum of the light source is obtained. In contrast, the resin coating absorbs certain wavelengths of the incident light (indicated by drops in intensity), resulting in a characteristic resin spectrum.

2.2 Raman spectroscopy

Raman spectroscopy is an analytical technique that provides information about molecular vibrations and interactions, chemical structure, phase, polymorphism and crystallinity. Using this method, a sample is irradiated with a suitable laser light source. This produces a small amount of Raman scattered light (inelastic scattering), which is recorded by a CCD camera as a Raman spectrum. The characteristic patterns in a Raman spectrum then allow the identification of substances/components. The measurement requires only small sample volumes and is fast, non-contact (exception: Raman immersion probes) and non-destructive. Raman spectroscopy enables the analysis of solids, powders, liquids, gels, slurries and gases in the form of pure substances, mixtures and solutions. The materials can be inorganic, organic and biological. Compared to IR spectroscopy, the method can also be used without restriction for aqueous solutions. Raman spectroscopy is an established laboratory method, but its use directly in the process ("inline") is still a relatively new field. The main reason for this is that Raman signals are comparatively weak and can be negatively influenced by several factors such as fluorescence of the sample, background illumination or too high temperatures.

When light is scattered by matter, almost all of the scattering is an elastic process (*Rayleigh scattering*) and there is no change in energy. As a result, Rayleigh scattered light has the same wavelength as the incident light. Only a very small percentage of scattering is an inelastic process, resulting in an energy difference between incident and scattered light. This effect is known as *Raman scattering* and arises from molecular vibrations causing a *change in polarizability*. In standard Raman measurements, the Rayleigh scattered light is rejected using a filter and only the so-called *Stokes Raman scattering* is recorded for simplicity. Stokes Raman scattering is a process in which an electron is excited from the ground level and falls to a vibrational level. It involves energy absorption by the molecule and hence this type of scattered light has less energy (i.e. a longer wavelength) than the incident light.

Laser wavelengths ranging from UV through visible to near infrared can be used for Raman spectroscopy. The choice of laser wavelength, λ, has an important impact on experimental capabilities, since the Raman scattering intensity is proportional to λ^{-4}. Therefore, an (infra-)red laser results in a decrease in scattering intensity by a factor of 15 or more, when compared with blue/green visible lasers. On the other hand, 785 nm is the only wavelength that is directly accessible via a long-lived diode. Apart from this, red and near infrared lasers are good for fluorescence suppression.

Each peak appearing in a Raman spectrum corresponds to a specific molecular bond vibration, including individual bonds (e.g. C-C, C=C, N-O, C-H) and groups of bonds. According to the picture on the right, the peak position provides information about the molecular structure and thus enables the identification of the substance. At least in the case of a homogeneous sample, the peak height is linear in concentration. Any residual stress inside the material can be evaluated from the direction and amount of any shift of the Raman peak. Whether there is much or little crystallinity can be read from the peak width.

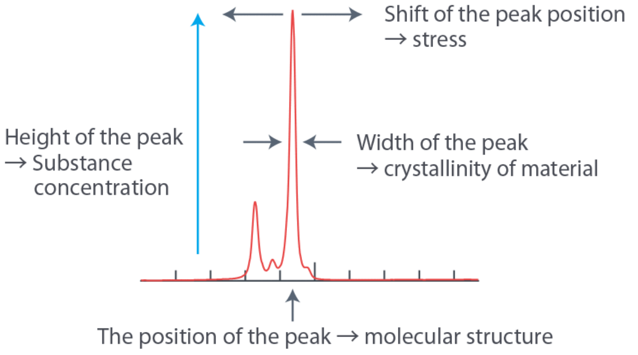

Figure 3. Chemical and physical information that can be obtained or extracted from a Raman peak. [1]

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[1] https://www.nanophoton.net/lecture-room/raman-spectroscopy/lesson-1-1, accessed in February 2024

2.3 Measurement setups

2.3.1 Setup for NIR measurements

A high-quality i-RED FTNIR process spectrometer in conjunction with fibre-coupled reflection optics was used for the measurements in the NIR range. The measuring principle was diffuse reflection. The samples were illuminated with halogen light sources. The light reflected from the sample surfaces was collected via an optical fibre and forwarded to the process spectrometer. An objective lens was used to improve the light coupling into the optical fibre. The illumination power, the measuring distance and the size of the measuring spot on the sample surface generally depend on the choice of the optics. In the present case, 4 halogen lamps with 10W each, a measuring distance of approximately 80 mm and a measuring spot size of about 23 mm were used. For practical reasons, the reflection optics was mounted on the vertical axis of a gantry robot. In order to compensate for inhomogeneities in the samples, to minimise thermal input, and to carry out automated multi-point measurements, the samples were scanned in a meandering pattern by moving the x-y table (sample table) of the robot. A scheme and a photo of this measurement setup are shown in *Figure 4*. However, as part of the method development, some measurement series were also carried out at rest or with a rotary table for sample movement (which was placed on the x-y table beneath the optics).

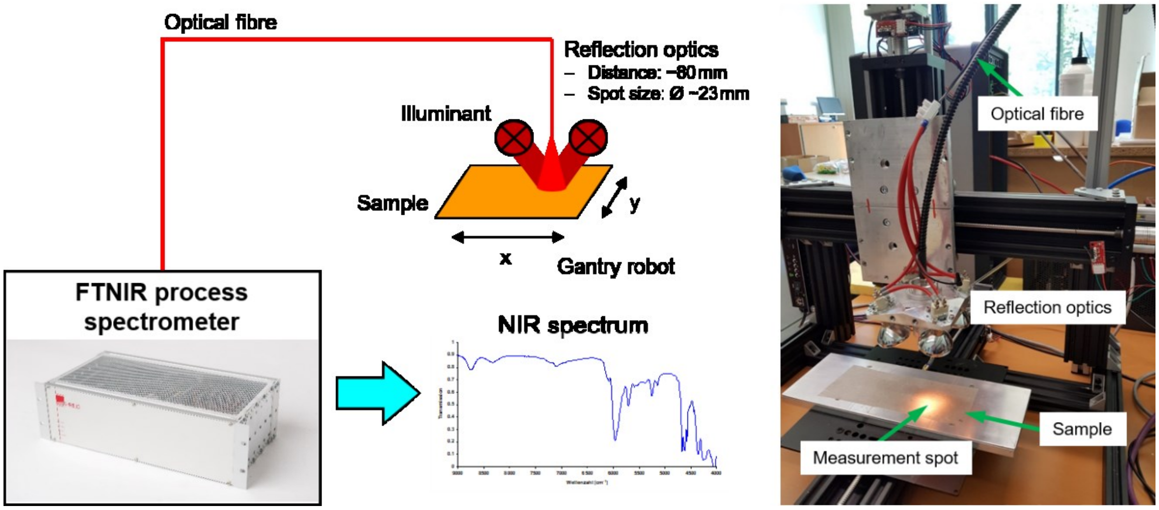

Figure 4. Measurement setup for the FTNIR spectroscopic analysis of glass fibre composite components in the laboratory.

2.3.2 Setup for Raman measurements

The Raman measurements (measuring principle: Raman scattering) were carried out using an i-RED Raman process spectrometer in conjunction with a fibre-coupled Raman probe from Wasatch Photonics. For this purpose, the individual samples were excited with a laser beam (wavelength: 785 nm). The scattered light was collected by the probe, guided through an optical fibre to the spectrometer and registered by a CCD camera as a Raman spectrum. The measuring distance (12 mm) was defined by the Raman probe, the spot size on the samples was approximately 1 mm. The laser power was chosen to maximise the Raman signal without destroying the samples or generating too much fluorescence. For multi-spot measurements, each sample was placed on the x-y stage of a gantry robot and scanned according to a pre-programmed path. The measurement setup is shown in the following figure.

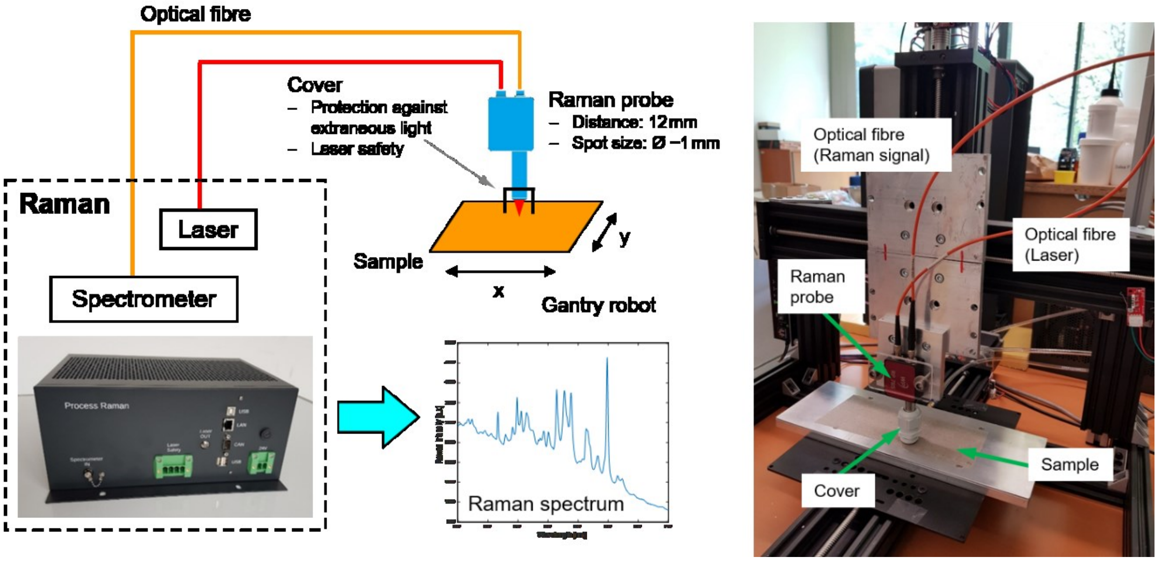

Figure 5. Measurement setup for the Raman analysis of glass fibre composite components (small-scale implementation in the lab).

3. EXPERIMENTAL RESULTS

3.1 NIR analysis of glass fibre composites

3.1.1 Analysis of vitrimeric resins and polyester resins

The **3R resin** developed by CIDETEC in the project is an **amine-based epoxy vitrimer**. It is obtained by using the (commercially available) amine-based dynamic hardener 4-aminophenyl disulfide (AFD), which creates reversible crosslinks in the polymer matrix. Fibre-reinforced polymer composites (FRPCs) fabricated with this resin can be reshaped at the end of their service life and processed into new parts by applying heat and pressure. For recycling it is therefore important to identify parts that are suitable for re-shaping.

Figure 6 shows the NIR spectra of three cured 3R resin samples provided by CIDETEC. The samples represent different 3R resin formulations. They contain different epoxy monomers (pure DGEBA, pure DGEPPG, and a mixture of both), but all of them have been produced with the dynamic hardener AFD. The spectra were post-processed (1st derivative using a Savitzky-Golay filter) to remove unimportant baseline signals (offsets) and to improve the visibility of spectral differences between the samples. The figure shows that NIR signals can be received from all three samples and that the resins have many spectral features in common. Meeting these requirements is essential for the identification of the 3R resin by the NIR method.

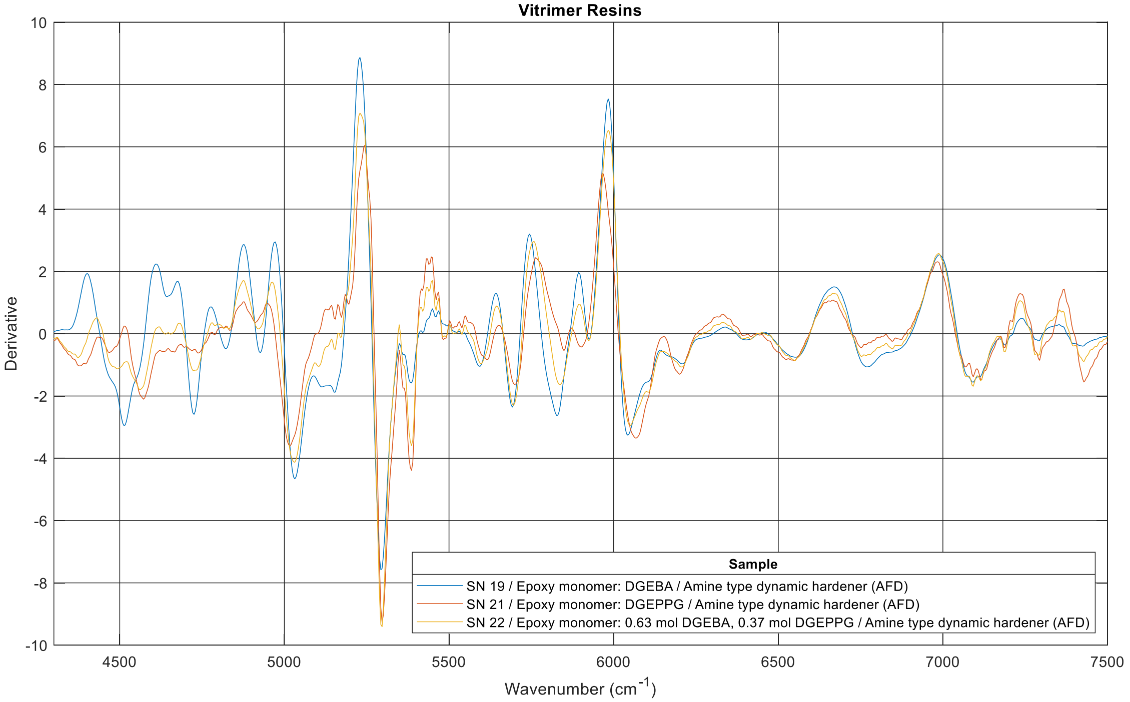

Figure 6. Post-processed (1st derivate) NIR spectra of three cured 3R resin samples provided by CIDETEC.

For the clear and unambiguous distinction of the 3R resin from other resin systems, each resin type requires characteristic features ("fingerprint regions"). In other words, differing spectral features have to be present in the spectral regime under consideration. In order to verify this, all other pure resin samples have been measured by the NIR method as well. While some of the samples consisted of cured resin pieces of different geometries, other resins had simply been filled into aluminium foil cups for curing. Apart from the 3R resin,

the following resin types or categories were available: (unsaturated) polyester resins, amine-based epoxy resins (= epoxy amines), and anhydride-based epoxy resins (= epoxy anhydrides).
Figure 7 shows the (post-processed) mean absorbance spectra of these 4 resin types. The mean spectra were calculated by averaging all resin spectra of the same category. For example, the vitrimer spectrum in this plot represents the mean spectrum of the individual 3R spectra shown in Figure 6. A Savitzky-Golay filter (1st derivative) was again used to remove unimportant offsets and to improve the visibility of spectral differences. Two of several characteristic spectral regions of the vitrimers are indicated by green boxes and are shown in more detail in Figure 8. From a spectroscopic point of view, the region above 6550 cm^{-1} shows significantly greater differences than the region at lower wavenumbers.

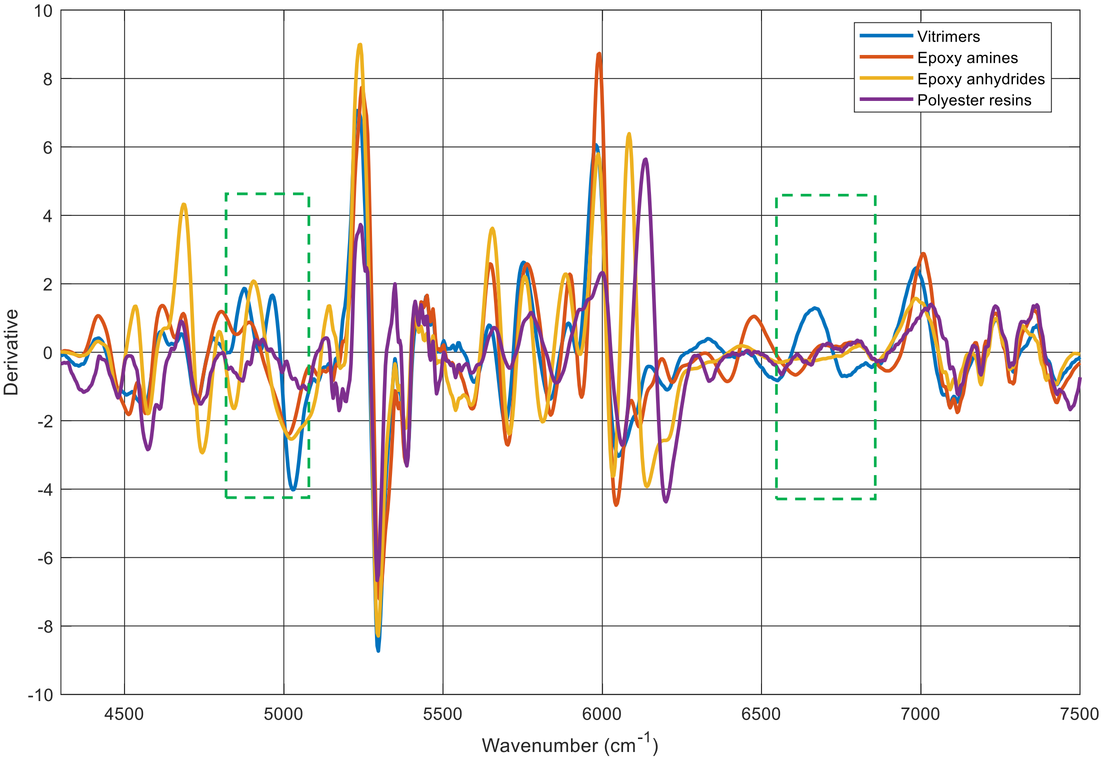

Figure 7. Comparison of the post-processed (1st derivative) mean absorbance spectrum of the vitrimers, epoxy amines, epoxy anhydrides and polyester resins. Two apparent "fingerprint regions" of the vitrimers are indicated by green boxes.

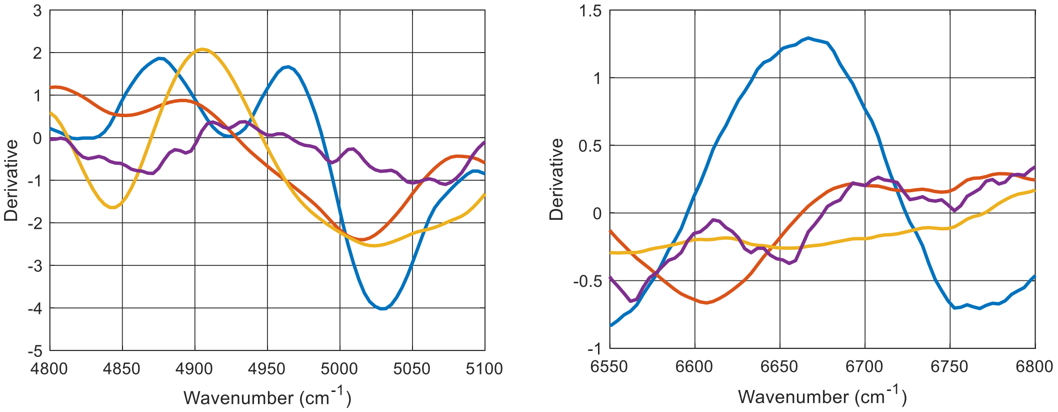

Figure 8. Characteristic spectral regions of the 3R resin (magnified).

CIDETEC also provided i-RED with an ordinary **thermoset** resin consisting of an epoxy monomer (DGEBA) and an amine-type non-dynamic hardener (DA). This thermoset resin is regarded by CIDETEC as a **reference sample** and should be able to be distinguished from the vitrimers spectroscopically. The following figures show that this is indeed possible. Figure 9 presents the (post-processed) mean absorbance spectrum of the thermoset in combination with the mean vitrimer spectrum from Figure 7. Figure 10 shows two larger spectral regions with several noticeable differences in more detail.

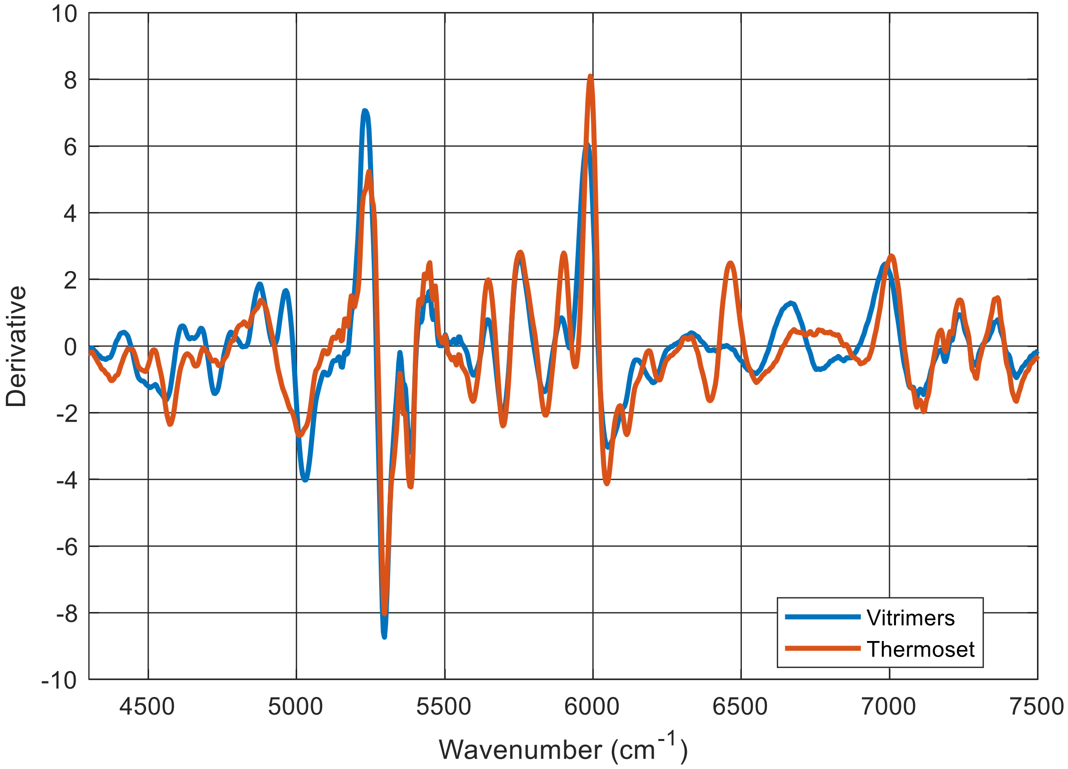

Figure 9. Comparison of the post-processed (1st derivative) mean absorbance spectrum of the thermoset with the corresponding mean spectrum of the vitrimers taken from Figure 7.

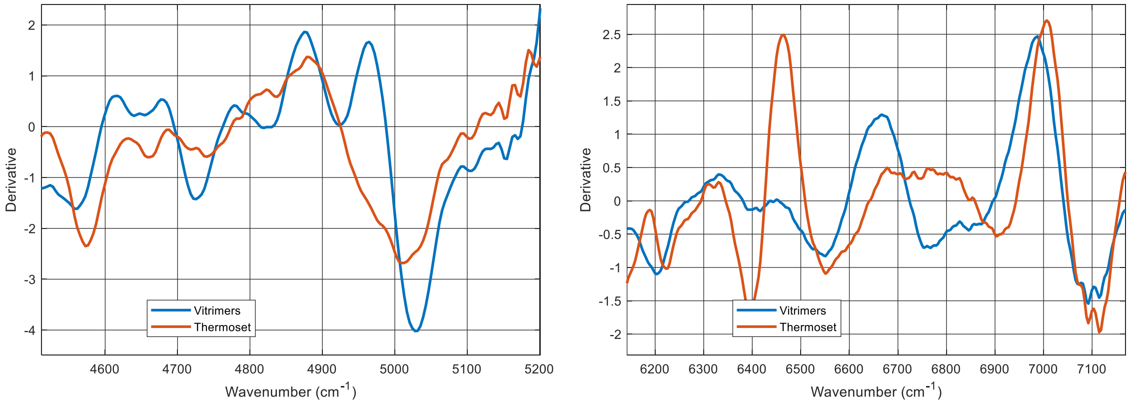

Figure 10. Two spectral regions selected from Figure 9 with several noticeable differences between the (post processed) mean absorbance spectrum of the thermoset resins and the vitrimers.

To illustrate the differences between vitrimeric and non-vitrimeric resins in another way, the measurement data was subjected to a **principal component analysis (PCA)**. With this analysis, spectral differences can be translated into spatial distances. The result is presented in Figure 11 and can be interpreted as follows:

1. Each individual symbol in the plot corresponds to a spectrum, each colour to a resin type.
2. Similar spectra / samples are grouped together (small distances between the data points), dissimilar spectra / samples have large distances from each other.
3. Groups (here: resin types) that do not overlap and hence can be separated from each other by drawing a circle or ellipse around them can be distinguished spectroscopically.

The PCA demonstrates, among other things, that CIDETEC's vitrimeric resins can be distinguished from all other resin systems under investigation using NIR spectroscopy. The next section discusses whether this also applies when the vitrimers are part of glass fibre composites.

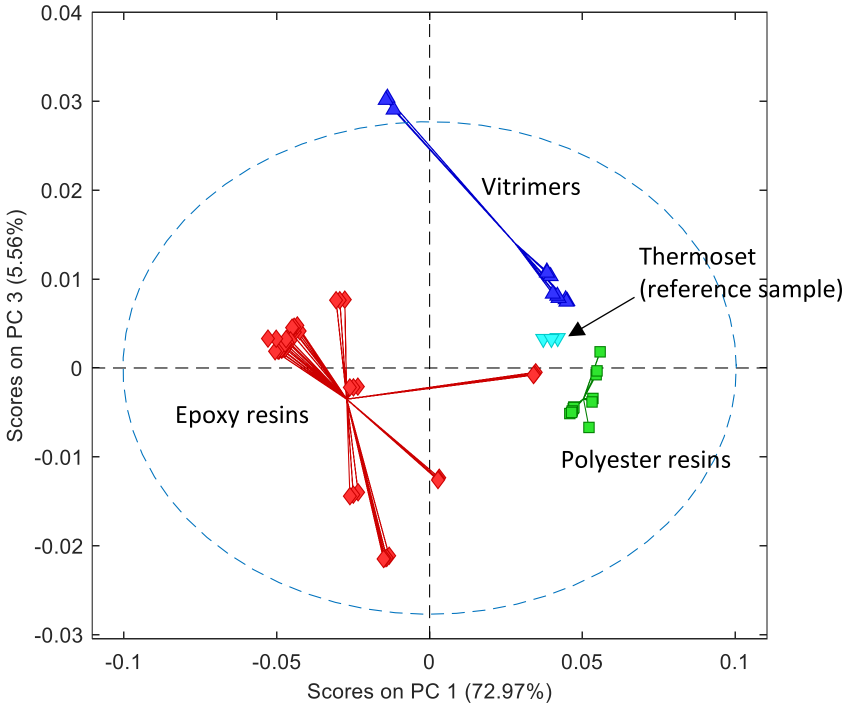

Figure 11. Result of a principle component analysis (PCA) for pure resins. The spectra of the vitrimers (dark blue) are separated from the other resins, i.e. do not overlap with them in this scores plot. This means that the vitrimer spectra differ sufficiently from the other spectra to allow identification with the NIR method.

Polyester resins:

Although it has not been explicitly mentioned so far, the above results for the vitrimeric resins also contain information on polyester resins. For example, Figure 7 shows a prominent feature (peak) at approximately 6150 cm^{-1} that is characteristic for the polyester resins. In addition, the PCA of the pure resin spectra in Figure 11 reveals that the spectra of the polyester resins group together, do not overlap with other groups and hence are clearly distinguishable from other resin systems. It can therefore be concluded that the NIR spectroscopic identification of pure polyester resins is possible.

3.1.2 Glass fibre composites made of vitrimers

Figure 12 shows the 1st derivative of two mean absorbance spectra. The first spectrum (red) was calculated by averaging all NIR spectra obtained from glass fibre composites made with a vitrimer. Three such samples were available. They were produced with different types of glass fibres (Twill 2x2 Vitrofiber RVS2/390/290, Twill 3x1 Chomarat G-WEAVE 780T3/1, and Chomarat G-PLY BX1200S T2,5), but with the same 3R resin formulation (Epoxy monomer: 0.63 mol DGEBA, 0.37 mol DGEPPG, hardener: AFD). This resin formulation was already used to prepare the pure resin sample SN 22, the spectrum of which is shown in Figure 6. The second spectrum in Figure 10 (blue) is the post-processed mean spectrum of all other available glass fibre samples. It comprises the individual spectra of samples made of (unsaturated) polyester resins and vinyl ester resins. In addition, it contains a sample with unknown resin system.

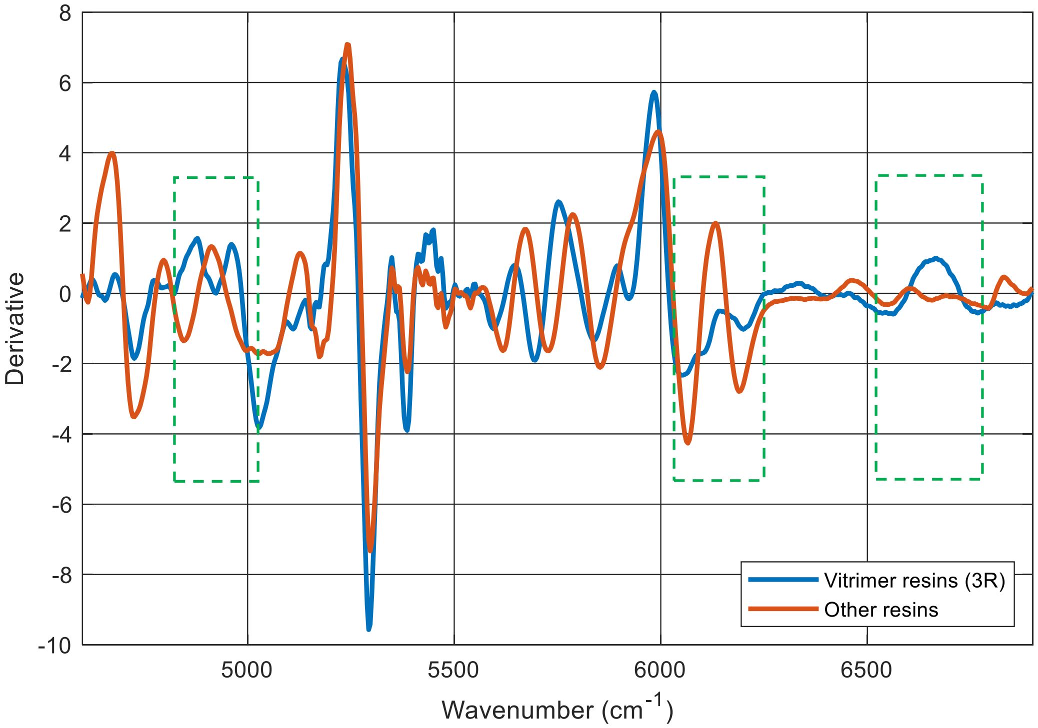

Figure 12. Post-processed mean absorbance spectra of the vitrimer samples (blue) and all other available glass fibre composite parts (red). The latter spectrum comprises the individual spectra of samples made of polyester resins and vinyl ester resins, but also the spectrum of a sample with unknown resin system.

A comparison reveals that the two characteristic regions of the pure vitrimeric resins, which are indicated by green boxes in Figure 7, are also present in the resin spectra on glass fibres. This important result cannot be taken for granted. First, certain fibres can significantly influence / alter the NIR spectra of a resin matrix (e.g. due to excessive absorption). Although it was to be expected that this would not be the case here (as glass is transparent to light in the near-infrared range), it had to be checked explicitly. Second, some of the glass fibre samples have been produced with resins that were either not available as pure resins (e.g. the vinyl ester resins) or could not be specified. It was therefore necessary to examine whether or not these resin systems show similar spectral features to the vitrimers in the areas in question. In addition to the 2 spectral regions mentioned before, Figure 12 reveals a further region at around 6150 cm^{-1} that seems to be characteristic for the 3R resin. (In Figure 7, the importance of this area can only be recognised with great difficulty.)

From the above results, it can be concluded that it is possible to identify the 3R resin using NIR spectroscopy even when it serves as the matrix of a glass fibre composite component. This assessment is supported by the following Figure, which shows the result of a PCA of the measurement data (NIR spectra of all glass fibre parts).

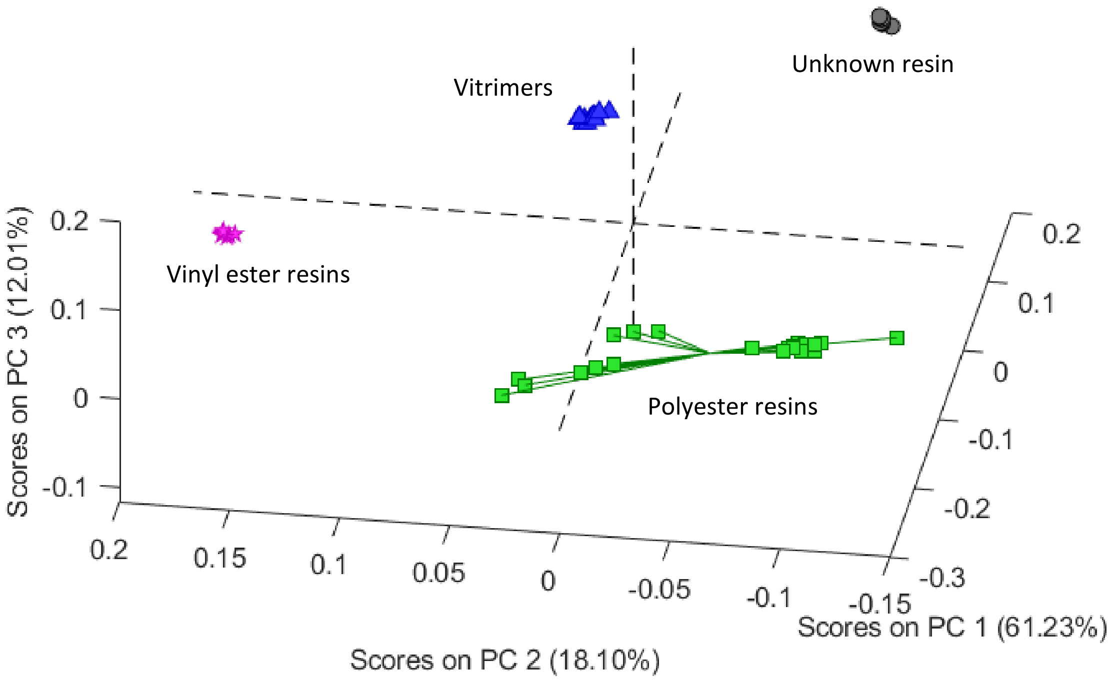

Figure 13. Result of a principle component analysis (PCA) based on the NIR spectra of all available glass fibre parts. The spectra of the parts with vitrimers (dark blue) are clearly separated from the spectra of the other composites in this 3D plot. This means that the vitrimer samples differ sufficiently from the samples with other resin system to allow identification with the NIR method.

3.1.3 Glass fibre composites made of polyester resins

The possibility to clearly distinguish glass fibre composites with a polyester resin matrix from samples with other resin systems via the NIR method can already be deduced from the PCA result (see Figure 13): the samples with polyester resins form a group that is clearly separated from all other resin groups in this three-dimensional plot.

Another insight can be gained from a direct comparison of the individual absorbance spectra, as shown in Figure 14. In the spectral range between 6000 and 6200 cm^{-1}, a prominent feature can be recognised that is characteristic for the polyester resins and enables their clear identification. For a better overview, the corresponding mean absorbance spectra are shown in Figure 15.

However, it should be pointed out that, in contrast to the vitrimers, it is possible to recognise such resins without having to post-process the spectra accordingly. This means that no detailed analysis (e.g. the use of a 1st derivative) is required to make the spectral differences stand out clearly, and also indicates that the NIR spectroscopic identification of glass fibre parts with polyester resins is a measurement task that is much easier to accomplish than with vitrimers.

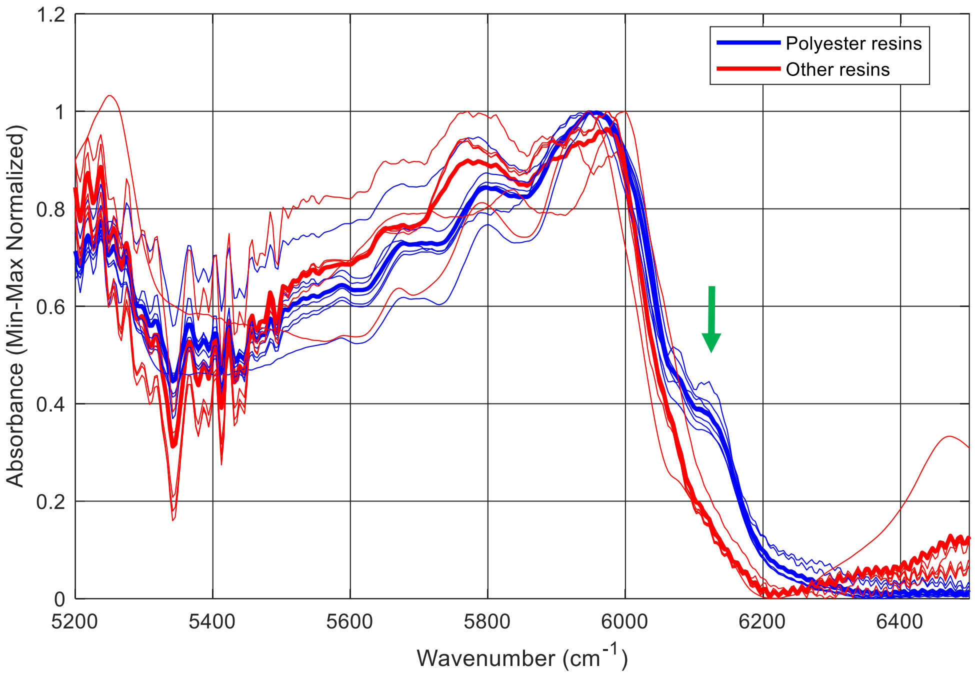

Figure 14. Individual absorbance spectra of the glass fibre samples with polyester resin matrix (blue) and of all other available glass fibre samples (red). A characteristic feature of the polyester resins in the region between 6000 and 6200 cm^{-1} is indicated by a green arrow. This spectral feature enables the clear identification of glass fibre parts made with such resins.

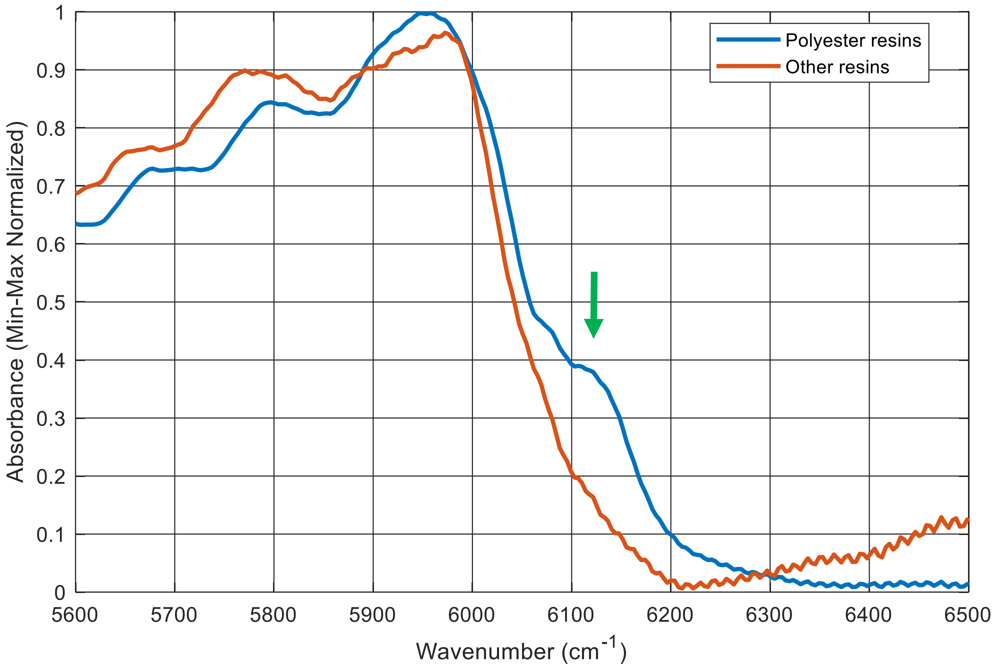

Figure 15. Comparison of the mean absorbance spectrum of the samples with polyester resin matrix (blue) with the corresponding spectrum of all other glass fibre parts (red). Both spectra have been obtained by averaging the individual spectra shown in Figure 14. The spectral feature characteristic for the polyester resins is again indicated by a green arrow.

3.2 Raman analysis of glass fibre composites

All Raman spectra shown in this section have been obtained using the measurement setup in Figure 5, but with an important difference: the entire setup was placed in a black-lined and light-proof "tent" to minimise stray light. The Raman spectra of the vitrimeric resins (samples SN 19, 21 and 22) are shown in Figure 16. In addition, the graph contains the spectrum of the thermoset provided by CIDETEC as a reference (SN 20).

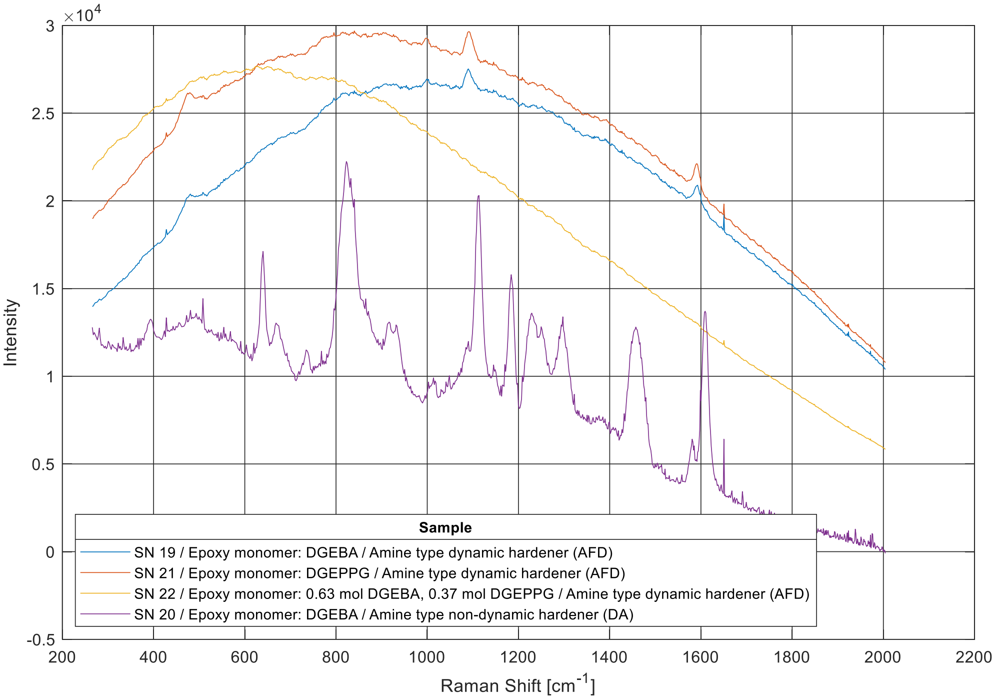

Figure 16. Raman spectra of the vitrimeric resins and of the thermoset reference sample. While the Raman signals are clearly visible in the thermoset spectrum (and would allow identification of this material), strong fluorescence is obtained from each of the three 3R resin formulations.

It can be seen from the figure that only very unspecific Raman signals (and hence small peaks) are obtained from the vitrimers. In addition, significant fluorescence is detected in each case, as indicated by the strong curvature of the spectra. In contrast, the Raman peaks of the thermoset are clearly visible and would allow this material to be identified unambiguously. For glass fibre composites containing a CIDETEC vitrimer the situation is even worse: the Raman peaks are barely recognisable and mainly fluorescence is detected (see Figure 17).

In order to achieve stronger Raman signals, a lower laser excitation wavelength would be appropriate, but a shorter wavelength corresponds to a higher energy input and would increase the fluorescence even more. It must therefore be concluded that Raman spectroscopy is not a suitable choice for identifying glass fibre composites with an 3R resin matrix.

Comparable results were achieved with many other glass fibre composite parts and resin systems, with the exception of composite materials with a polyester resin matrix. As can be seen in Figure 18, although these glass fibre samples also fluoresce to a considerable extent, the Raman signals are still clearly recognisable. This is the prerequisite for identifying the resin system of such parts using the Raman method. However, the difficulties encountered with other glass fibre composites, the promising results obtained using the NIR method and the fact that the use of lasers in industrial plants is associated with many restrictions, make the Raman method unattractive for the intended application.

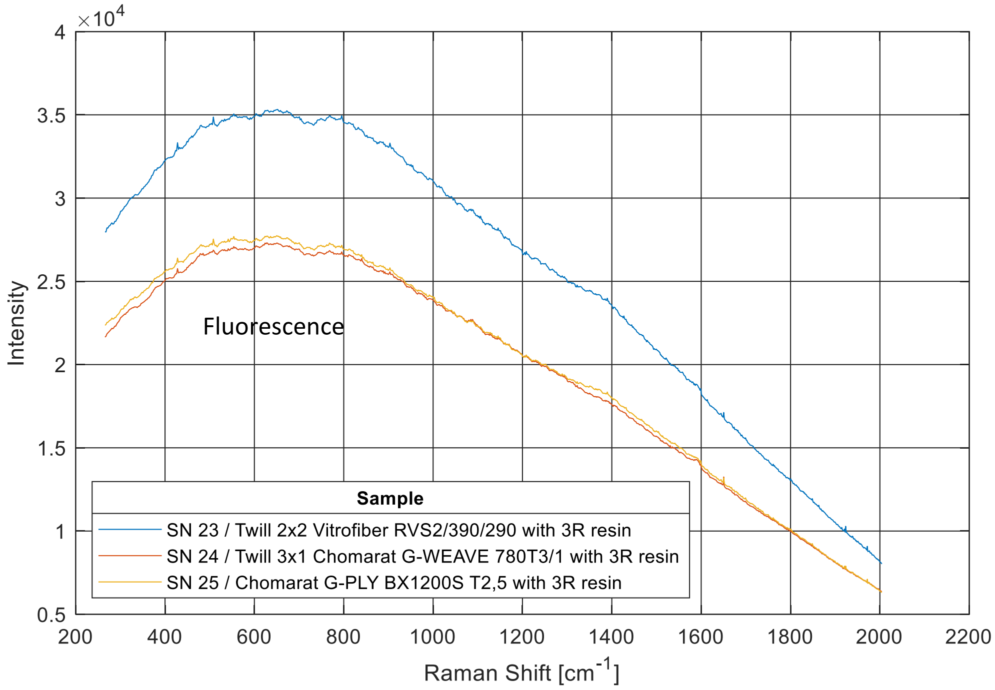

Figure 17. Raman spectra of three glass fibre parts containing different types of fibres, but the same 3R resin formulation (Epoxy monomer: 0.63 mol DGEBA, 0.37 mol DGEPPG, hardener: AFD). As the spectra mainly show fluorescence, it is not possible to identify the resin system.

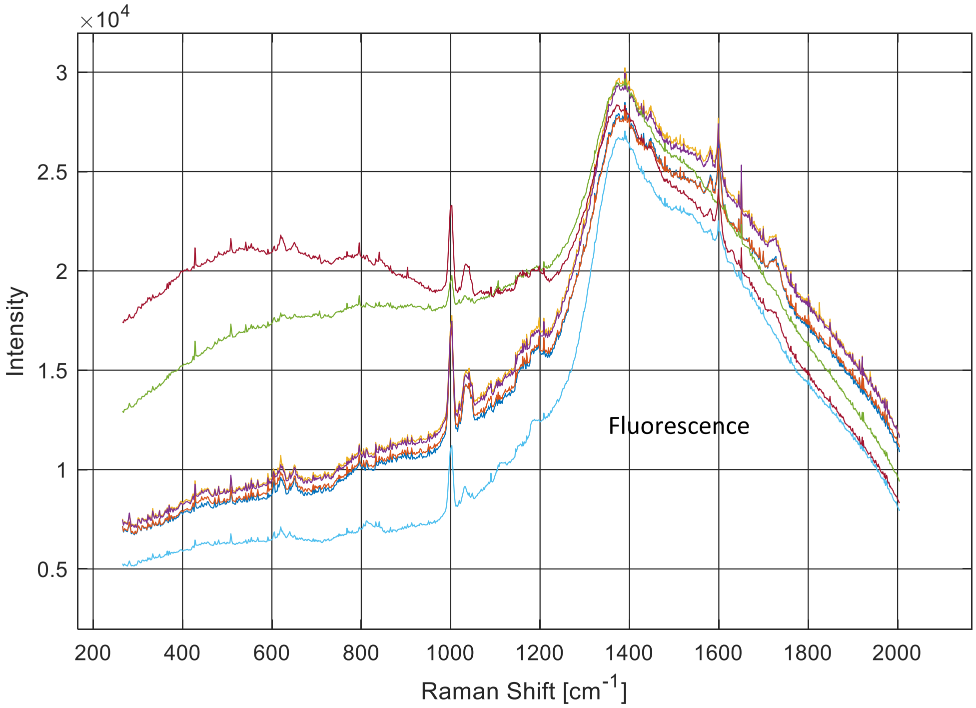

Figure 18. Raman spectra of the glass fibre samples with polyester resin matrix. Although these samples fluoresce to a considerable extent, the Raman signals of the resin are still clearly recognisable and would allow its identification.

4. SORTING OF GLASS FIBRE PARTS

The basic requirement for mechanical sorting is a reliable *in-line material recognition*. In the experimental study conducted by i-RED, *near-infrared (NIR) spectroscopy* was found to be the most promising approach for the identification of the resin system of glass fibre composite components, particularly the identification of parts made of polyester resins and CIDETEC's 3R resin (vitrimer). In this section it is discussed, how the automated classification and sorting of such parts could actually be carried out *on a large scale*, i.e. in an industrial *sorting plant*.

The result of an NIR spectroscopic measurement on a material is a so-called NIR spectrum of this material. In the case of non-transparent substances, it is obtained by feeding the light reflected from the material surface to a spectrometer, an optical instrument that decomposes the light into its spectral components, and outputs the reflected intensity as a function of the wavelength (or a comparable spectroscopic quantity such as the wave number). For material identification, the measured NIR spectrum is then compared with already known spectra (by applying a so-called classification model/algorithm). The result of this analysis is subsequently used for mechanical sorting. The entire sorting process therefore consists of the following 3 three sub-steps:

1. Spectra generation (spectroscopic measurement)
2. Spectra evaluation (material identification and classification)
3. Mechanical sorting

The NIR method has a number of advantages that make it an indispensable tool for the inline analysis of materials and substances in industrial plants. These include the fact that the method is non-destructive and easy to automate, permits high measurement speeds, and enables contactless measurements as well as the use of glass waveguides (to reach inaccessible areas of a plant). Furthermore, the method allows great flexibility in the choice measurement optics, is harmless to humans (since no laser radiation is involved), is insensitive to ambient/extraneous light, and usually does not require sample preparation.

The idea of using spectroscopic techniques to assist in recycling processes is not new. For example, such methods are already being used on a large scale for material identification and sorting in plastics recycling. Today's plastic sorting systems often use *hyperspectral cameras* for material detection. In hyperspectral analysis, NIR spectra are recorded on objects moving in the y-direction, using a line scan camera positioned in the x-direction (perpendicular to y). In this way, each image point or pixel is ultimately assigned a single spectrum. The recorded spectra form a 3D data set or cube of the form (x, y, λ), which can be evaluated in real time using special mathematical methods. This makes it possible to assign a specific material class to each pixel, provided the camera has been calibrated accordingly beforehand. However, the experimental results of i-RED clearly show that such cameras are not suitable for identifying the resin systems of glass fibre composite components because of their low resolutions and their limited spectral ranges. Instead, it is necessary to use a high-quality (FT)NIR process spectrometer with high resolution that covers the entire near-infrared spectral range.

The use of process spectrometers for material recognition requires *(multi-)point measurements* on the glass fibre waste parts. Figure 19 illustrates how such measurements can be performed on a large scale. Optical cameras determine the positions of the parts on a conveyor belt. This position is then transmitted to a delta robot on which the NIR reflection optics is mounted. This type of robot can move very quickly and enables rapid measurement and therefore also a large throughput of components.

A classification model is required to identify the resin systems in the glass fibre parts. It must be created in advance, but can be continuously improved during operation, for example through the use of AI methods. The model should be stored in a spectrometer with an integrated chemometrics engine so that it can be applied directly "on board" to the measured spectra.

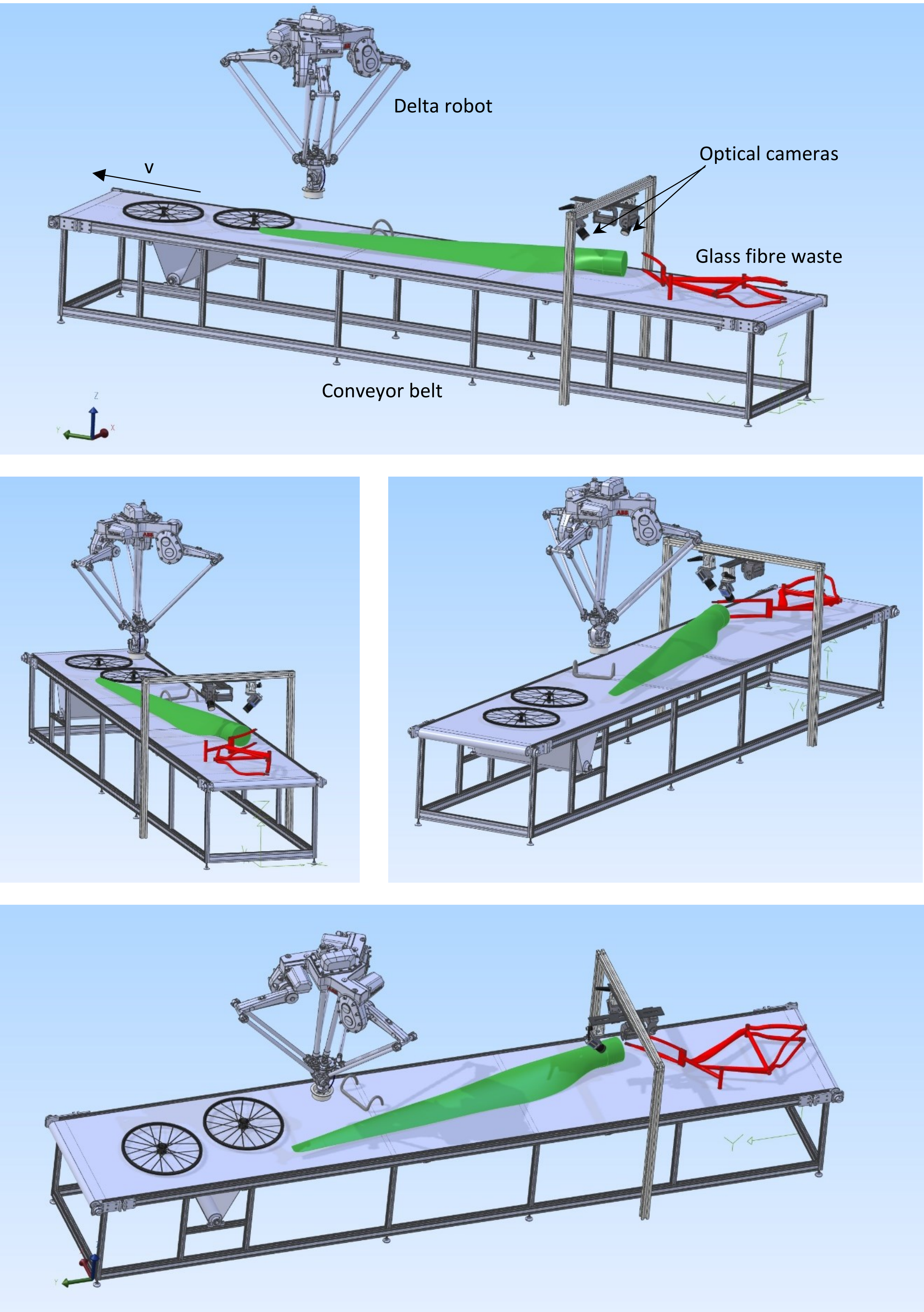

Figure 19. Industrial concept for the spectroscopic identification of glass fibre composite waste according to its resin system.

To create an initial resin classification model, a sufficient number of spectra recorded on glass fibre parts with known resin system are, for example, subjected to a *partial least-squares discriminant analysis (PLS-DA)*. This classification method is used in chemometrics to analyse and optimise the separation between different groups of samples by linking the two data matrices X (raw data, spectra) and Y (class memberships, groups). PLS-DA can be viewed as an adaptation of the well-known PLS regression method to the problem of *supervised clustering*. Supervised models are built using prior knowledge about sample features, e.g. membership of material groups. This explains, why the creation of a classification model requires reference materials with known composition.

Once a glass fibre part has been classified according to its resin system, the corresponding classification result is forwarded to the control system of a pneumatic sorting unit in the form of a suitable electrical signal. In the case of larger components, the signal can alternatively be transmitted to a robot with a gripper arm. The sorting unit or robot then carries out the fractionation.

It is important to note, however, that the NIR method has also some limitations. For example, the spectral features of the resin systems can no longer be reliably detected by this method when the composite parts are humid or wet (e.g. due to temporary outdoor storage). This is, because water has its strongest absorption bands in the infrared spectral range. As a result, only dry or dried parts should be analysed. Another influencing factor is the limited penetration depth of IR radiation into materials. The resin system of completely painted and/or coated parts can therefore generally not be analysed using this spectroscopic technique. For this reason, such coatings must be removed at least in places prior to analysis, provided the parts have no larger free area without coating. A future approach in this context could be the development of paints and coatings that are transparent for light in the NIR spectral regime ("transparent-to-spectroscopy" or "spectroscopy-friendly" paints and coatings). The process steps and material flow in a sorting plant for any uncoated fibre composite waste is shown in Figure 20.

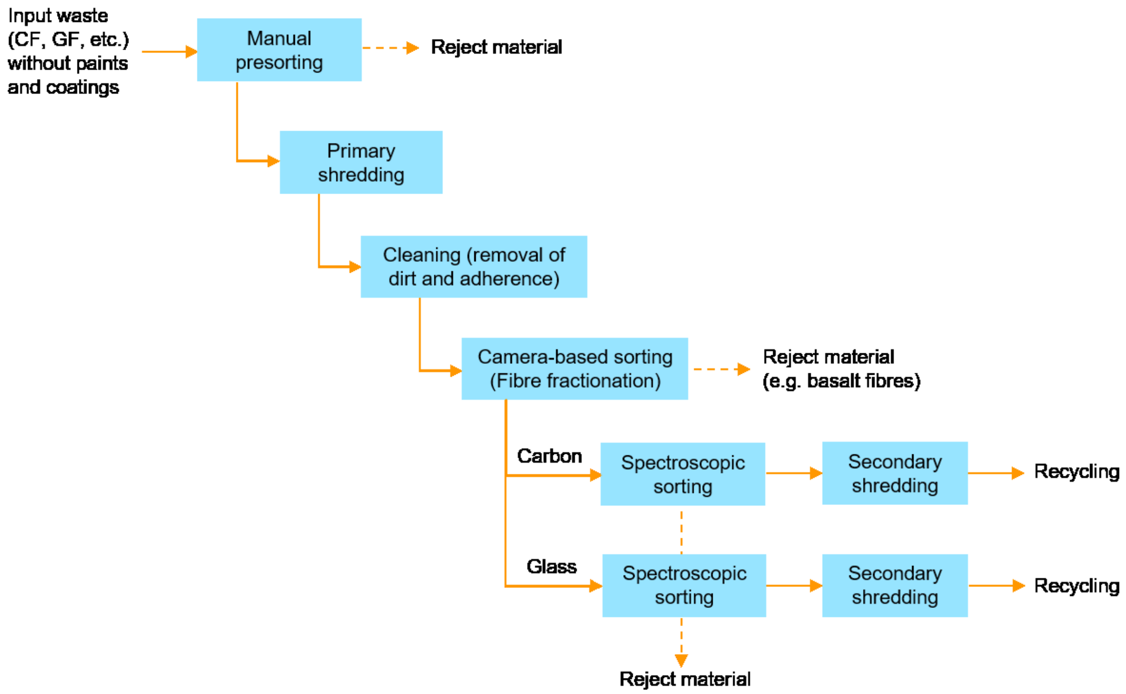

Figure 20. Process steps and material flow in a future sorting plant for uncoated / unpainted fibre composite waste.

5. SUMMARY & CONCLUSIONS

The MC4 long term circular approach for glass fibre composite materials is based on the use of an amine-based epoxy vitrimer ("3R resin") developed by CIDETEC as part of the project. Composites fabricated with this resin can be reshaped at the end of their service life and processed into new parts by applying heat and pressure. For recycling, it is therefore important to identify parts that are suitable for re-shaping. In the course of an experimental study conducted by i-IRED, near-infrared (NIR) spectroscopy was identified as the optimum method for this task. It could be shown that the NIR spectra of glass fibre parts produced with the 3R resin contain several spectral features and regions that are characteristic for this particular resin type and thus enable its unambiguous identification.

It was also demonstrated that glass fibre composites with a polyester resin matrix can be clearly and easily distinguished from parts containing other resin systems via the NIR method. This is, because the NIR spectra of polyester resins contain a characteristic feature in the spectral range between 6000 and 6200 cm^{-1} that can be used to identify these resins. This finding is important for the MC4 short term circular approach for glass fibre waste, which is based on the reuse of shredded glass fibre parts as a core or filler material in new parts.

The classification / sorting of glass fibre waste on a large-scale requires (multi-)point measurements using an (FT)NIR process spectrometer with high resolution that covers the entire NIR spectral range. This can be implemented using a delta robot with mounted NIR reflection optics in conjunction with a camera system to determine the position of the waste on the conveyor belt. The fibre composite parts are differentiated according to their resin system by employing a spectra classification model that has been created in advance using a partial least-squares discriminant analysis (PLS-DA), for example.