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

MC4 101057394

Multi-level Circular
Process Chain for Carbon
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Deliverable D3.3: Sorting method for carbon fibre parts

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Contributions by: -

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SEN	Sensitive information	

Contents

1. INTRODUCTION & OBJECTIVE

In order to avoid a significant amount of **carbon fibre (CF)** waste at the production stage, the short-term circular approach of the MC4 project is based on the re-use of waste material before it is being cured. More precisely, technologies are developed that enable the re-use of cut-off materials in new parts or in roll material as an intermediate product. The long-term objective is to develop a **chemical recycling process** for cured waste and end-of life parts that causes minimal damage to the fibres and enables them to be re-used as yarns, rovings, mats and fabric through spinning and weaving processes. This recycling approach includes the separation of matrix (resin) and fibre, and is economically feasible due to the high cost of virgin carbon fibres.

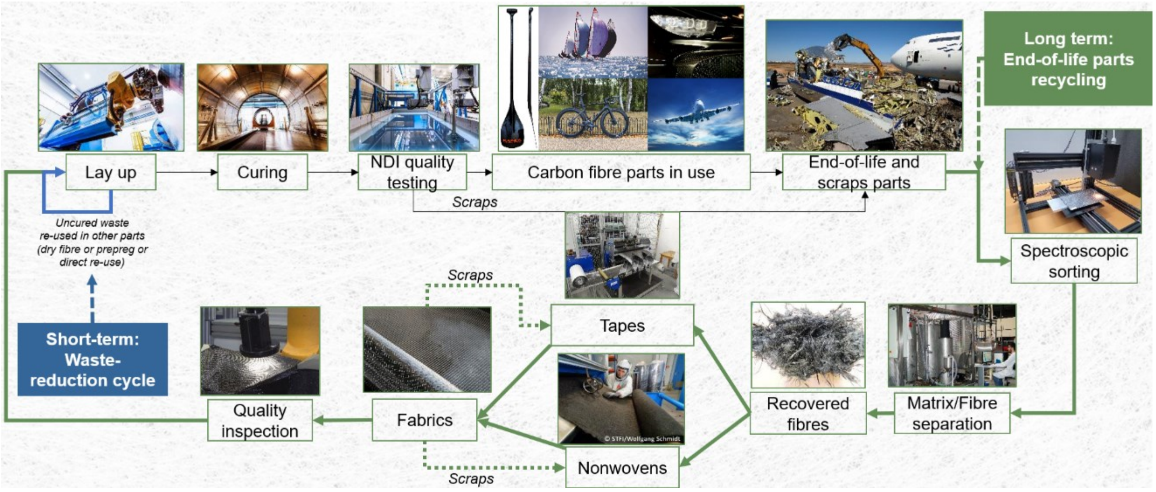

Figure 1. Circular process for carbon fibre composite parts. MC4 aims at a "short-term" and a "long-term" recycling process.

The chemical recycling process for the matrix/fibre separation of carbon fibre composite components is being developed by GAIKER within the project and focuses on **epoxy resins with amine hardeners**. To make sure no other resins enter into the chemical processing, the parts need to be **sorted** based on their chemical composition. This is, because other resin systems, especially epoxy anhydrides, would negatively influence or disrupt the chemical process.

The basic requirement for mechanical sorting is a reliable **material recognition**. In order to avoid damaging the materials, a **non-destructive** analysis is needed. In addition, the analysis method should be fast and easy to automate. This explains the preference for optical methods, in particular techniques of **molecular spectroscopy**. 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. However, the recycling of carbon fibre composites has not yet benefited from these technological developments. This is most likely due to the fact that such materials have rarely been recycled to date, and when they have, no procedures have been used that require material identification and sorting prior to processing. One of the main tasks of the MC4 project is to finally change this.

The method for material recognition was developed by i-RED as part of the project. The aim was to study on a laboratory scale, which spectroscopic methods and measurement setups (optics, illumination, spot size, measurement distance, etc.) are best suited for the non-destructive identification of the resin type of carbon fibre composite parts. The investigation was carried out with the help of partners who provided sample parts and materials (GAIKER, FIDAMC, Managing Composites, Amura, NOMA, and 2 partners from another project). The challenge here was to obtain sufficient signal / information from the samples, as carbon fibre materials are black in colour and therefore reflect very little light.

2. METHODOLOGY

2.1 Samples

The development of any spectroscopy-based method for material recognition/identification/classification requires **reference samples** of known composition. In order to collect suitable samples, i-RED provided the project partners with a list of specific material requirements. The description included information on the type of material needed, the material size and geometry, the resin system and surface coatings. The main specifications are listed below.

a) Material type: The source and age of the carbon fibre composites materials were of minor importance, e.g. they could be waste parts or leftovers from production, they could have just been newly manufactured or be at the end of their life cycle. In addition, it was considered advantageous to carry out measurements on cured resin pieces and liquid resin components.

b) Material size and geometry: For technical reasons, the size of the solid samples should be between about 5 x 5 cm and 50 x 50 cm. Their shape was of secondary importance, but flat samples were preferred. For liquid samples, a volume of at least 100 ml was defined.

c) Resin system: Only resin systems that have been analysed spectroscopically can be reliably detected or identified later on. The aim was therefore to achieve a high degree of variability in the resin systems (different resins, hardeners, additives and catalysers), but with the focus on epoxy resins with amine and anhydride hardeners.

d) Coatings: Ready-to-use fibre composite parts are often coated with painted finish or PET. For the analysis both coated and uncoated samples were needed. If an uncoated version was not available for a particular part, that part should have at least one area where the colour or surface coating has been completely removed.

e) Sample descriptions: In addition to the above requirements, the partners were asked to provide as complete sample descriptions as possible (fibre type, fibre quality, resin type, hardener type, coating, origin and former intended use of the part, etc.).

Collecting suitable samples for method development was a time-consuming process with several pitfalls. First, it turned out that the transport and dispatch of liquid resin samples is associated with great difficulties for safety reasons. The investigation therefore had to be limited to solid samples (which was, however, not a real disadvantage). Second, there were limitations regarding the availability of samples made of certain resin systems, especially samples with epoxy anhydrides. Material sources outside the MC4 project thus had to be found. Third, the resin system of several CF parts could not be fully specified by the supplying partners. This was particularly the case with prepreg samples, i.e. components made from pre-impregnated fibres. The main reason for this is that prepreg manufacturers often develop their own resin systems, but keep the composition secret. Even with the help of the safety data sheet of the prepreg (if accessible at all), it was often not possible to deduce the exact resin type. Such unspecified samples could therefore not be used for method development.

It is to be expected that the digital product passport will solve (or at least alleviate) the problem of unknown material specifications in the future. In some cases, this digital tool could even circumvent the need for material analysis and sorting. In general, however, this will not be the case as carbon fibre waste must be delivered to the recycling plant in pre-shredded and/or compressed form (for transport reasons) and could be mixed with other materials.

2.2 Infrared spectroscopy

Infrared (IR) 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 globars or halogen lamps), different *vibrational modes* of the molecules are excited in a sample by absorbing the light. The light reflected or transmitted by the sample is then decomposed in a spectrometer, an optical device that works as a "light analyser", resulting in a characteristic IR spectrum. IR spectra can be used to identify the types of molecules and to determine chemical and physical parameters. With the IR method, a wide range of substances (gases, liquids, solids, granular materials such as powders) can be analysed quickly and non-destructively, and it is possible to determine many different parameters (concentrations, layer thickness, pH value, degree of curing, etc.) simultaneously and in real time from a *single* spectrum.

In IR spectroscopy, two spectral regimes play a major role: the **mid-infrared (MIR, 3 – 50 µm)** and the **near-infrared (NIR, 0,78 – 3 µm)**. In the mid-infrared spectral range, the *fundamental* vibrations of molecules are revealed. As the natural frequencies are characteristic for the individual molecule types, the corresponding peaks in the absorption spectrum allow their identification, while the area below the peaks is associated to their concentration. In the near-infrared range, the *combination and overtone vibrations* of the molecules or functional groups are excited. As a result, the peaks are much wider and overlap, making 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 the industrial environment than the mid-infrared for physical and technical reasons. 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.

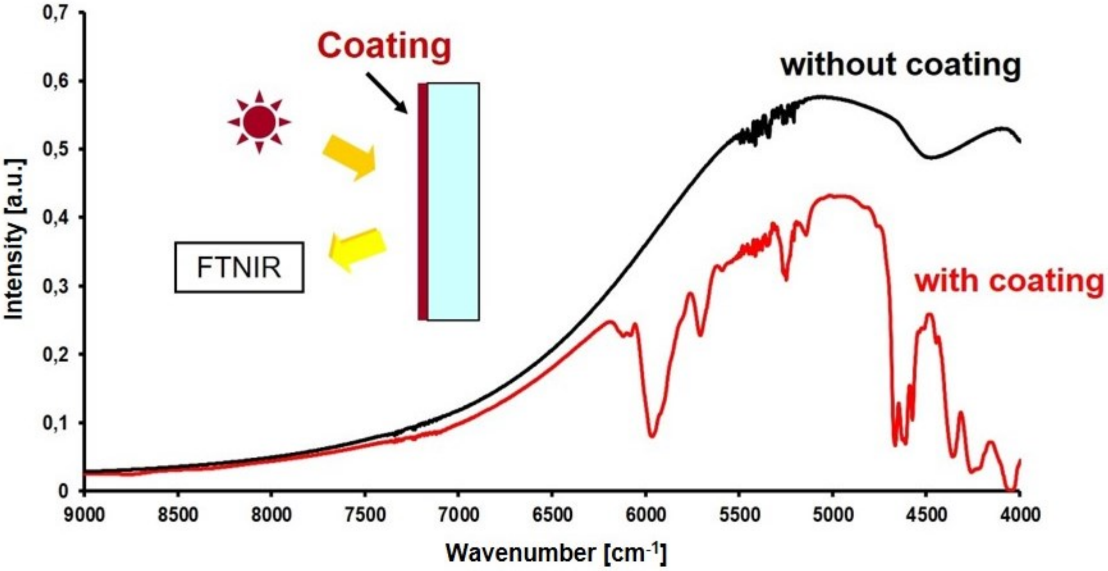

Figure 2. Principle of an IR reflection measurement shown on a metallic sample with and without resin coating. As the pure substrate reflects the incident light freely, a spectrum of the light source is measured. In contrast, the resin coating absorbs certain wavelengths of the incident light (indicated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

2.3 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. In contrast 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.

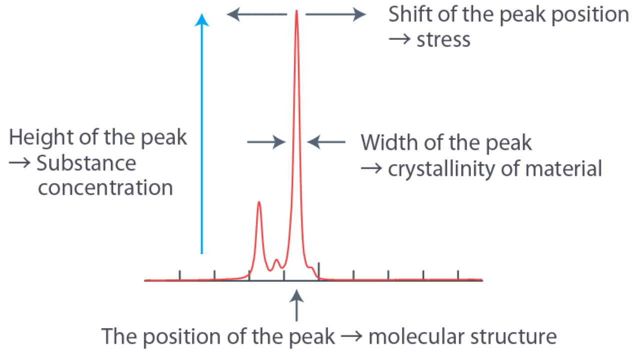

Figure 3. Chemical and physical information that can be obtained or extracted from a Raman peak. [1]

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

2.4 Comparison of the measurement methods

The following figure and table provide a brief overview of the individual measurement methods and enable a quick comparison of the approaches.

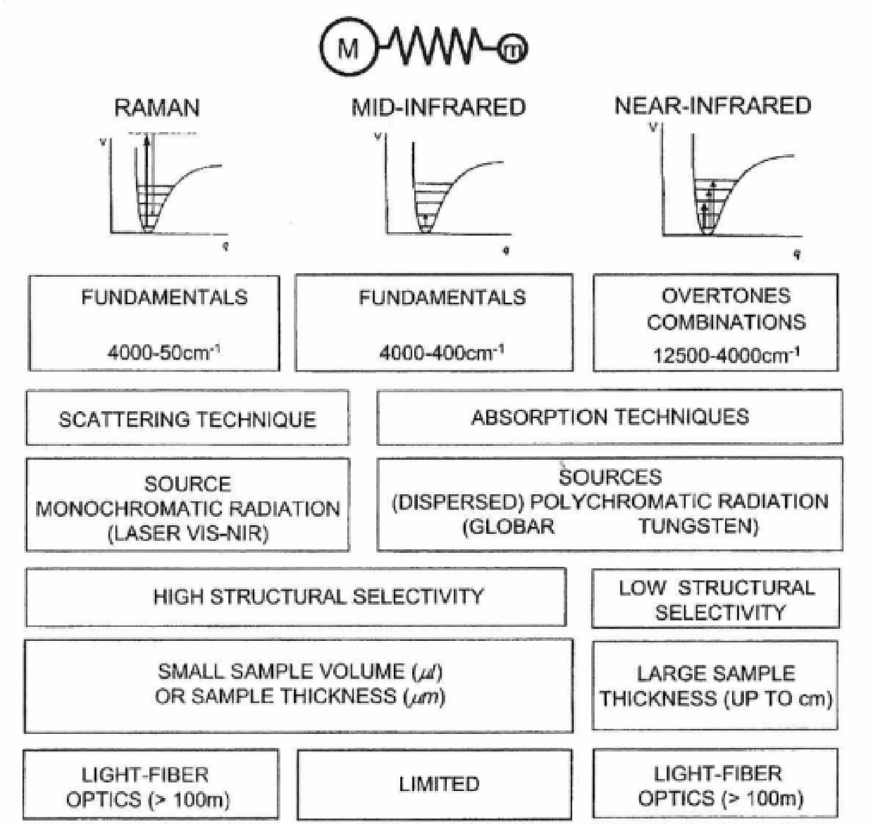
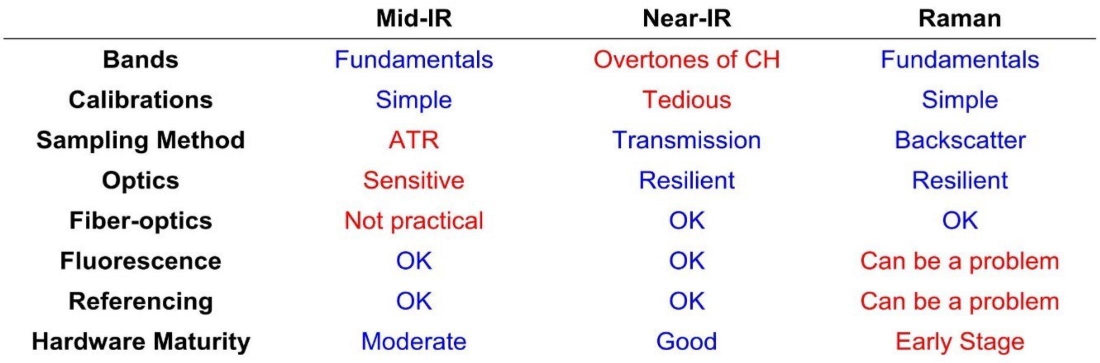


Figure 4. Comparison of Near-Infrared, Mid-Infrared and Raman spectroscopy. [2]



	Mid-IR	**Near-IR**	**Raman**
Bands	Fundamentals	Overtones of CH	Fundamentals
Calibrations	Simple	Tedious	Simple
Sampling Method	ATR	Transmission	Backscatter
Optics	Sensitive	Resilient	Resilient
Fiber-optics	Not practical	OK	OK
Fluorescence	OK	OK	Can be a problem
Referencing	OK	OK	Can be a problem
Hardware Maturity	Moderate	Good	Early Stage

Table 1. Advantages and disadvantages of Mid-IR, Near-IR and Raman process spectroscopy. [3]

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[2] H. W. Siesler et al.: Near-Infrared Spectroscopy: Principles, Instruments, Applications; 1st edition, Weinheim 2002

[3] W. M. Doyle: COMPARISON OF NEAR-IR AND RAMAN ANALYSIS FOR POTENTIAL PROCESS APPLICATIONS, Axiom Analytical Technical Note AN-922, IFPAC-2001, Paper I-020, 2001

3. EXPERIMENTAL RESULTS

For the production of carbon fibres, a carbon-containing raw material is used, which is converted into graphite-like carbon using a chemical process. As a result, these fibres are black and have a characteristic gloss. The low reflectivity of dark materials poses a major challenge for spectroscopic analysis, regardless of the method used. For this reason, three different spectroscopic methods and different measurement setups were tested for the non-destructive identification of the resin type of carbon fibre composite parts. This section presents the measurement setups and the most important experimental results.

3.1 Application of NIR spectroscopy

3.1.1 Measurement setups

a) Stationary measurement setup

A high-quality i-RED FTNIR process spectrometer in conjunction with a 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 5. 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).

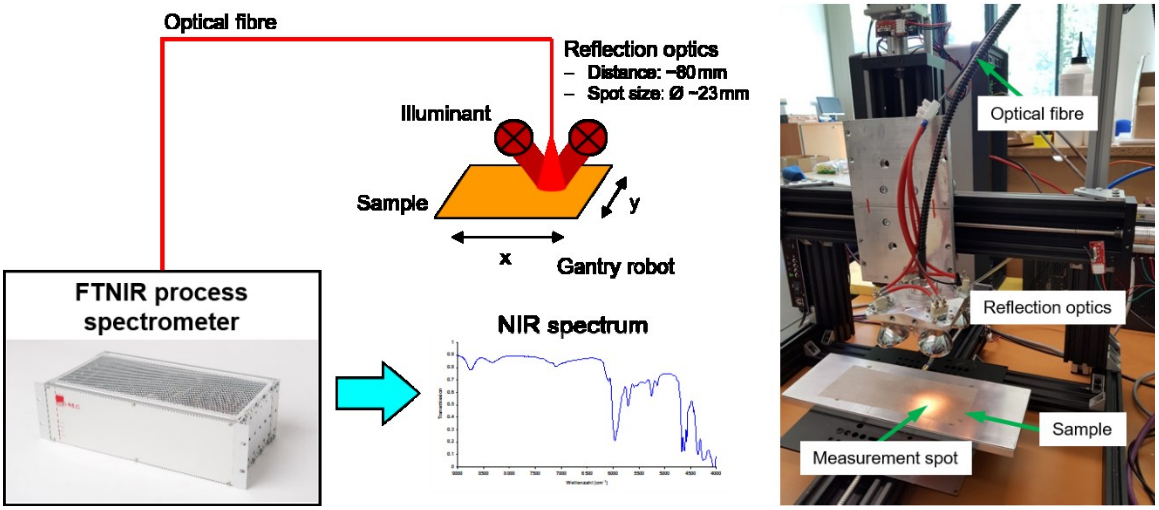

Figure 5. Stationary measurement setup for the FTNIR spectroscopic analysis of carbon fibre composite components in the laboratory.

Using the stationary setup it was possible to analyse all resin samples (cured resins) and CFRP parts, but in the latter case only weak signals were received. The signals were weak because there is only a thin layer of resin covering the fibres and because black materials are absorbing a large fraction of the light.

b) Optimised reflection optics (Handheld resin analyser)

In order to amplify the measurement signal, i-RED has developed an optimised reflection optics with an elliptical reflector (see Figure 6). This optics is placed close to the surface of the material to be measured, but can also be used in contact mode. A comparison with the conventional setup revealed that the amount of reflected light is increased by up to 20 times with the optimised system, while at the same time the measuring time can be massively reduced (to a few seconds). For demonstration purposes, this optics was later installed in a hand-held housing that is connected directly to the process spectrometer. It should be noted, however, that there is no need for a hand-held system or measurements in contact mode: several such optics could be combined to form a single reflection optics for non-contact measurements, provided the reflectors have been adapted to the desired measuring distance.

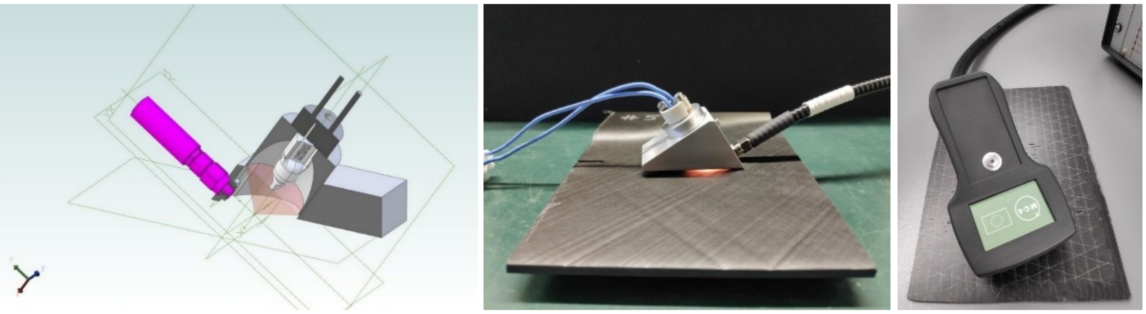

Figure 6. Left: 3D CAD drawing of the optimised reflection optics. Centre: Reflection optics (wedge-shaped component) during measurement on a CFRP plate. Right: Hand-held resin analyser (optics with housing); the measurement can be activated by pressing the circular button on the housing.

3.1.2 NIR analysis of pure resins

For better handling and easier measurement of the pure resins, they have been filled into aluminium foil cups by the supplier on behalf of i-RED. Figure 7 shows the NIR spectra of 10 different, completely cured epoxy resins with amine hardener (one spectrum per resin system). A comparison reveals that the spectra have many matching features. To make this easier to recognise, a so-called mean spectrum was calculated from the individual spectra and included in the graph (red, bold line). The matching peaks are an important prerequisite for the detection / recognition of such resin systems using the NIR method.

For a clear and unambiguous distinction between amine-based and anhydride-based epoxy resin systems, each resin system requires characteristic features ("fingerprint regions"). In other words, differing spectral features have to be present in the spectral regime under consideration. Figure 8 shows that this is indeed the case. Here, the mean spectra of both types of epoxy resins are plotted into a single graph, with some important differences marked by green arrows.

To illustrate the differences in another way, the measurement data was subjected to a principle component analysis (PCA). With this analysis, spectral differences can be translated into spatial distances. The result is presented in Figure 9. The graph can be interpreted as follows: similar spectra or samples are grouped together (small distances between the measurement data), while dissimilar spectra or samples have large distances to each other. The PCA demonstrates once again that pure epoxy amines and epoxy anhydrides can be clearly distinguished using NIR spectroscopy. The next section discusses whether this also applies when the resins are part of carbon fibre composites.

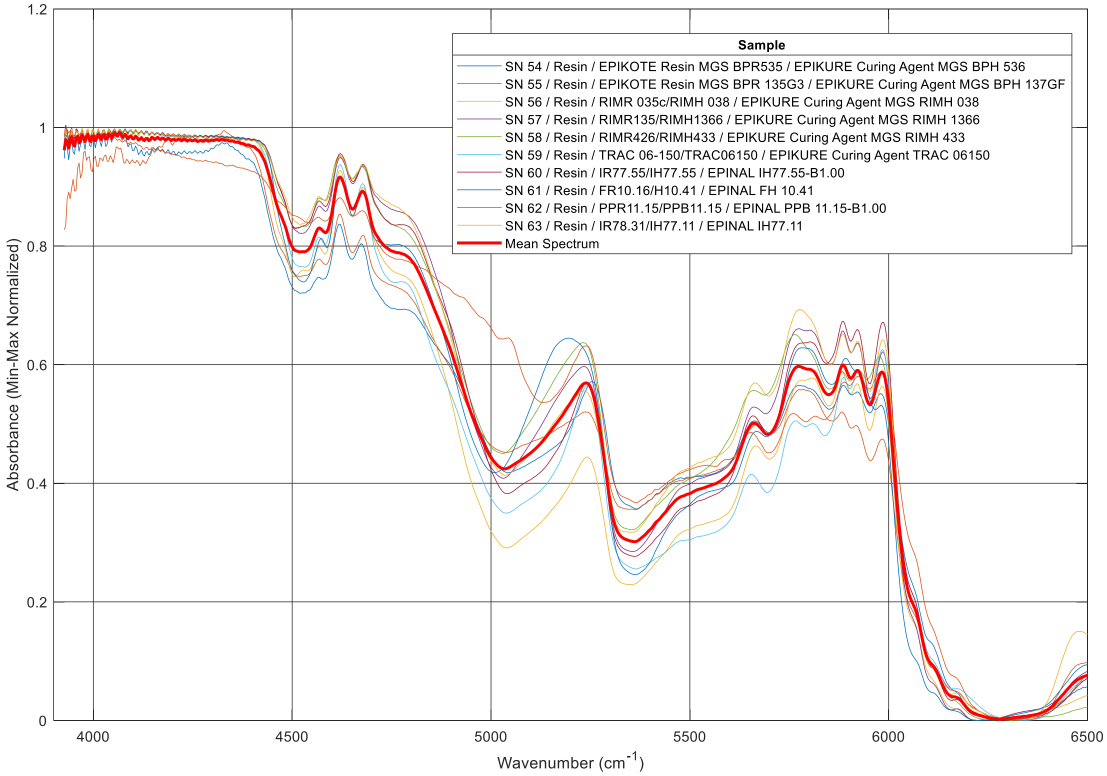

Figure 7. Normalized absorbance spectra of different amine-based epoxy resins.

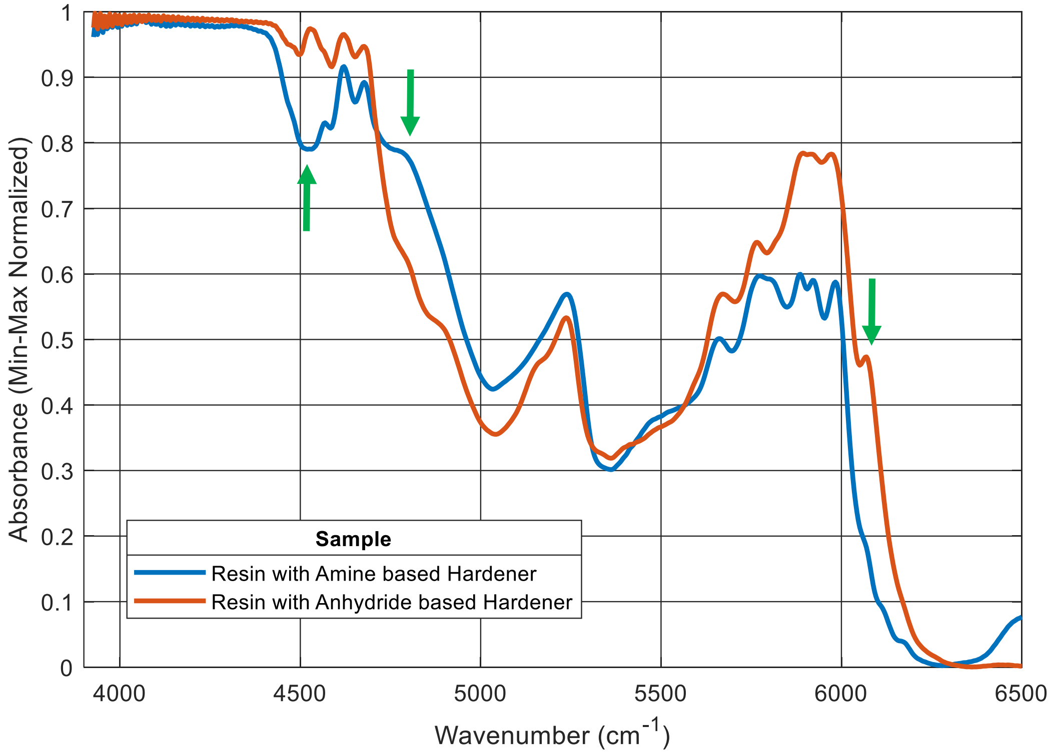

Figure 8. Mean absorbance spectra of the amine-based and anhydride-based epoxy resins. Important spectral differences are indicated by green arrows.

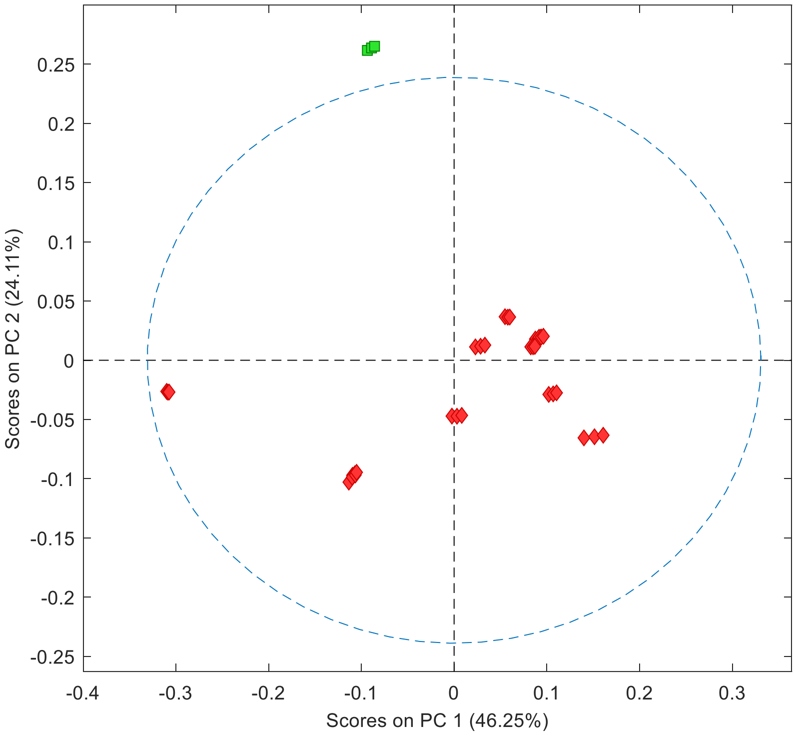

Figure 9. Result of the principle component analysis (PCA). The spectra of the amine-based (red) and anhydride-based (green) epoxy resin systems show a large spatial distance to each other in this scores-plot. This reveals that the spectra of these resin systems differ significantly.

3.1.3 NIR analysis of carbon fibre parts

Figure 10 shows post-processed NIR spectra of 16 different carbon fibre parts and prepregs made of epoxy amine resins (one spectrum per sample). All spectra have been recorded using the optimised reflection optics developed by i-RED. The red, bold line in the graph represents the mean spectrum. It was calculated by averaging the individual resin spectra. Figure 10 indicates two important facts: First, despite the low reflectivity of carbon fibre parts, sufficiently strong NIR signals could be received from these materials. This positive result can be explained by the use of the optimised measurement setup. Second, as with the pure resins, the spectra have many features in common, which is essential for a clear identification of epoxy amine resins on carbon fibres.

The clear and unambiguous distinction between amine- and anhydride-based epoxy resins again requires that the spectra of both resin types have characteristic, i.e. differing, features in the spectral regime under consideration. However, a direct comparison of the (mean) absorbance spectra, similar to Figure 8, did not provide a clear picture. A more detailed analysis then showed that it is necessary to post-process the spectra (first derivative) in order to recognise differences. The derivation of the mean absorbance spectra for both resin types is shown in Figure 11, with the most prominent differences indicated by green arrows.

Figure 12 presents the results of a PCA. Once again, the picture is not quite as clear as with the pure resins because some of the epoxy anhydride spectra are located in close vicinity to the epoxy amine spectra in the scores plot. On the other hand, the lack of overlapping of the two different classes of spectra indicates that a distinction between amine- and anhydride-based resin systems is possible even in the presence of weakly reflective carbon fibres. The PCA is therefore consistent with the previous findings.

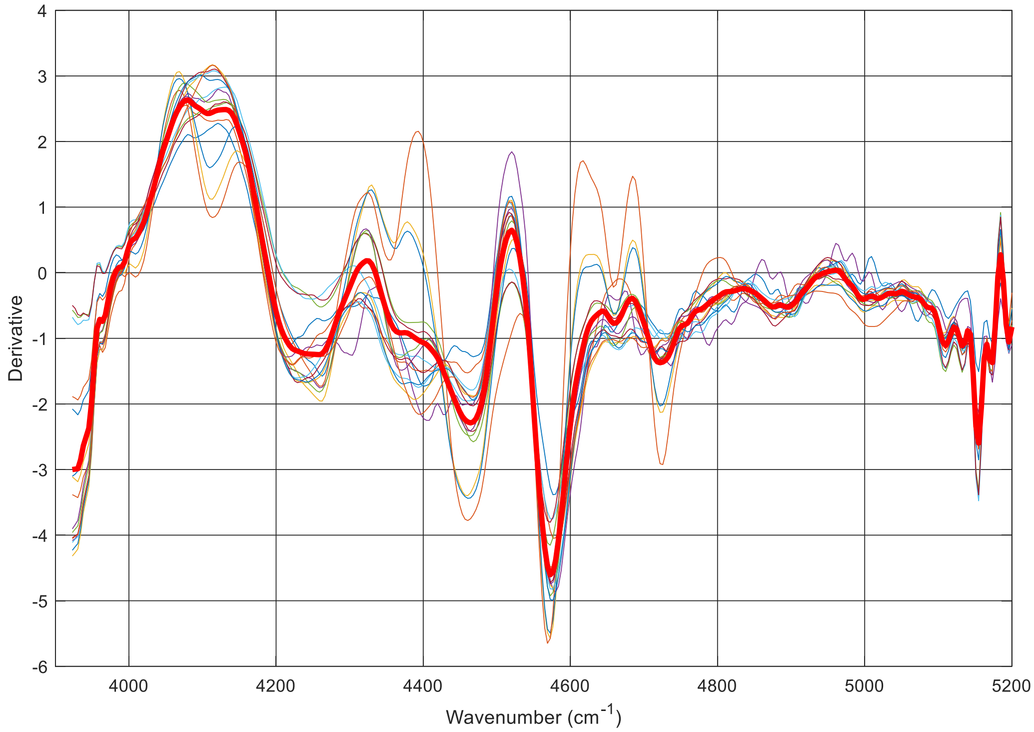

Figure 10. Post-processed NIR spectra (1. Derivative) of different amine-based epoxy resins on carbon fibres. The red, bold line represents the mean spectrum which was calculated by averaging all resin spectra. The legend with the sample descriptions has been omitted from the graph due to its length.

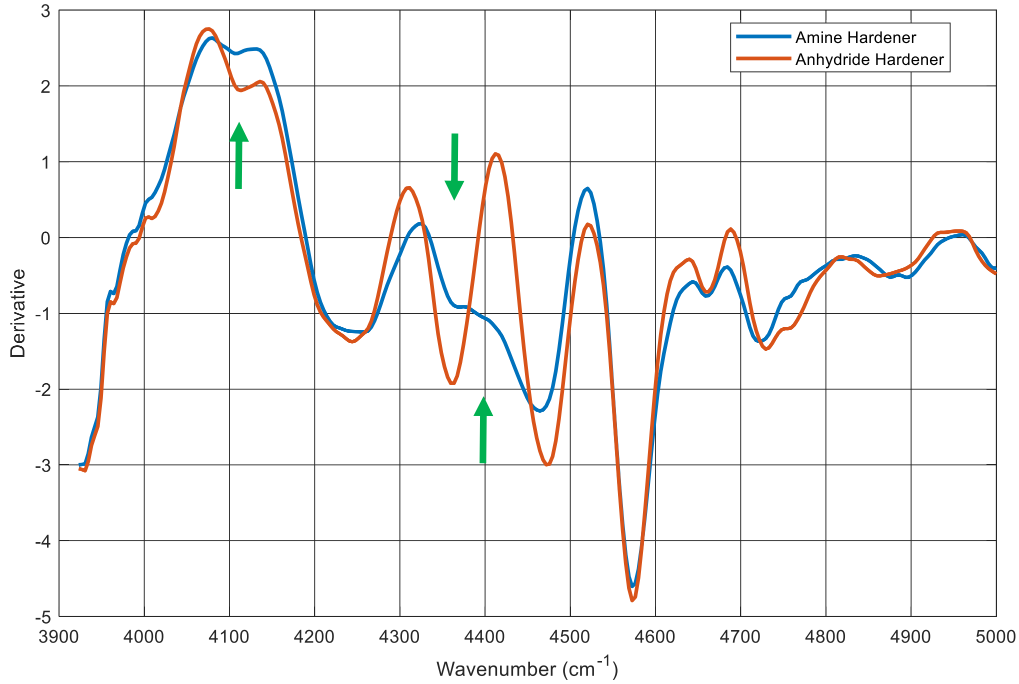

Figure 11. First derivate of the mean absorbance spectra of CF parts with amine-based and anhydride-based epoxy resin systems. The most prominent spectral differences are indicated by green arrows.

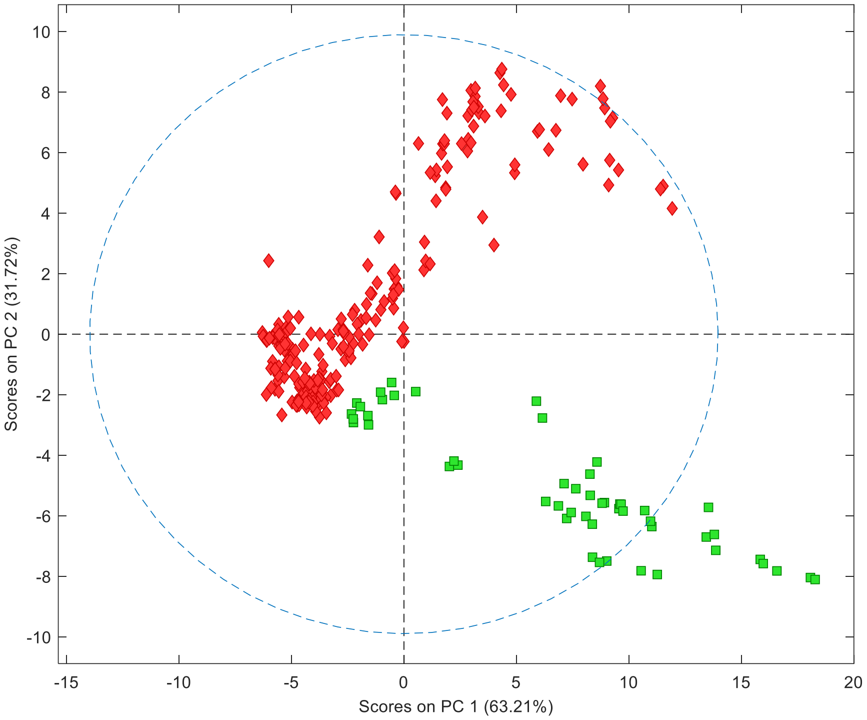

Figure 12. Result of the principle component analysis (PCA) for the spectra of CF parts with amine-based (red) and anhydride-based (green) epoxy resin systems. The distribution of the data points shows that the spectra corresponding to the same resin class often differ significantly from each other. On the other hand, the lack of overlapping of the two different classes indicates that a distinction between amine- and anhydride-based resin systems is possible.

A comparison of the above findings with the results of the other analysis methods (see Sections 3.2 and 3.3) reveals that the NIR method is the most promising approach for the non-destructive identification of the resin system of carbon fibre composites. This is encouraging because the NIR method has a number of advantages that make it particularly interesting for industrial application in a sorting plant. These include the fact that the NIR method is easy to automate, permits high measurement speeds, and enables the use of glass waveguides (to reach inaccessible areas of a plant) and optical switches (multiplexers). In addition, the method allows great flexibility in the choice measurement optics, is harmless to humans (because no laser radiation is involved), is insensitive to ambient/extraneous light, and usually does not require sample preparation. How the NIR method is actually employed for automated material classification is discussed in Section 4.

It is important to note, however, that there are 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 IR spectral range. As a result, only dry / dried parts should be analysed. Another influencing factor is the limited penetration depth of IR radiation into materials. The resin system of fully 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 area free of coating. A future approach in this context could the development of paints and coatings that are transparent for light in the IR spectral regime ("transparent-to-spectroscopy" or "spectroscopy-friendly" paints and coatings).

3.2 Application of MIR spectroscopy

An FTIR process spectrometer (developed by i-RED) in combination with an illumination optics consisting of 4 halogen reflector lamps of 20 W each was used for the analysis of carbon fibre composite materials in the mid-infrared spectral range. To increase the illuminance (radiant power) of the lamps, the front glass pane has been removed from each reflector. The light diffusely reflected from the sample surfaces was coupled directly into the spectrometer's interferometer as a free beam. The measurement setup is shown in the following figure. The measurement distance (from the optics) was approximately 120 mm, and the spot size on the sample was about 25 mm.

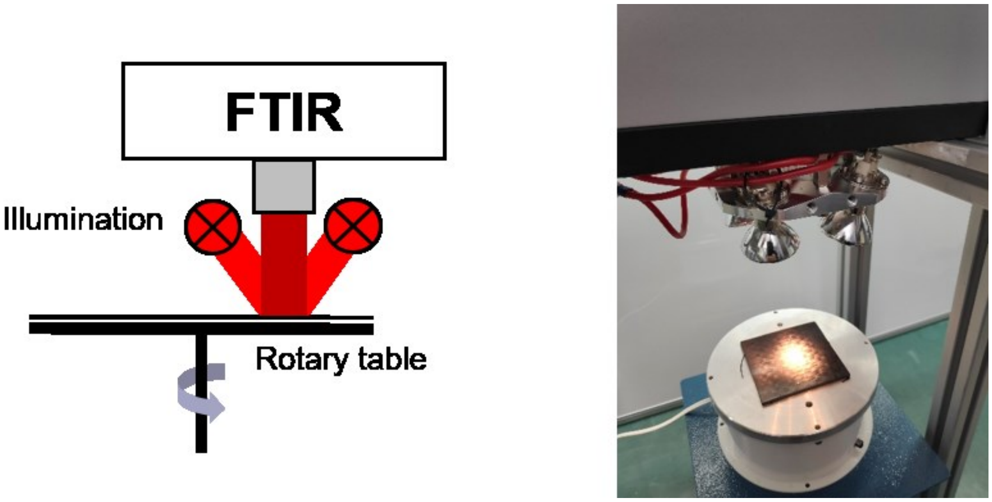

Figure 13. Laboratory setup for MIR spectroscopy of carbon fibre reinforced materials.

The spectra measured on CFRP components and prepregs with the above-described laboratory setup did not show any peaks characteristic for the resin systems of the respective samples, but only noise. This negative result can be explained by the poor reflectivity of black materials and the low penetration depth of the light in the MIR spectral range. In addition, it must be assumed that the illuminance (radiant power) of the halogen lamps used was still too low (e.g. because the infrared light is also absorbed by the glass of the halogen bulbs). This shows that the measurement setup is not suited for the intended application.

Alternative setups are unattractive, because they are not suitable for industrial use. For example, there is no way to overcome the limitation that so-called ATR probes, which are often used for lab applications, require very small measuring distances. Moreover, there is no possibility to use versatile glass waveguides in the MIR spectral regime, because infrared light is absorbed by glass. Instead, relatively short optical fibres made of special materials (e.g. chalcogenides) have to be used, but these are very brittle / fragile and greatly reduce the light output.

Due to the above-mentioned difficulties and the promising results obtained with NIR spectroscopy, the MIR approach was therefore abandoned. However, it is worth mentioning that MIR spectroscopy is increasingly being used for black plastics analysis in plastics sorting plants, as NIR spectroscopy has proven to be less suitable for such purposes. This demonstrates that black materials should not be lumped together: which spectroscopic method is appropriate for which black-coloured material must be investigated separately for each material class!

3.3 Application of Raman spectroscopy

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.

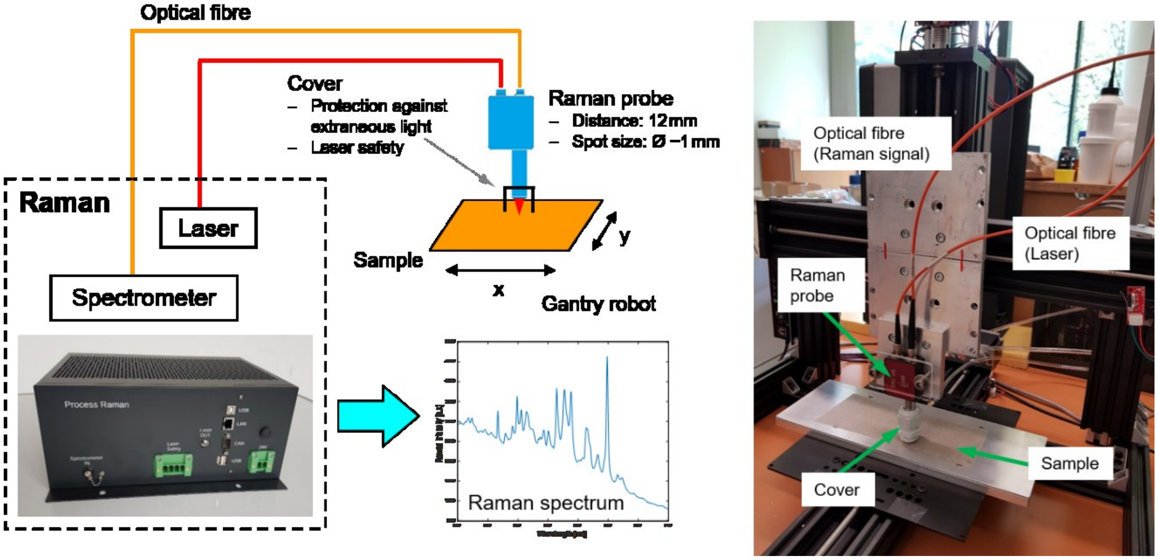

Figure 14. Measurement setup for the Raman analysis of carbon fibre composite components (small-scale implementation in the lab).

Figure 15 shows 2 Raman spectra recorded on a CFRP panel with an epoxy resin system. One measurement was taken in the centre of the plate (on resin on carbon fibres), the second measurement on a narrow strip of pure resin at the edge of the plate. It can be seen from the figure that only a very unspecific Raman signal is obtained on CFRP: the peaks that are obviously characteristic for the pure, cured resin are either not recognisable or only extremely weak in the resin spectrum recorded at the plate centre (on carbon fibres).

Comparable results were achieved with most of the other CF composite parts. In addition, in several cases a significant fluorescence was detected, which further masked the already weak Raman signals (see Figure 16). It must therefore be concluded that Raman spectroscopy is not a suitable method for analysing the resin system of carbon fibre materials, at least when using an excitation laser wavelength of 785 nm. In order to achieve stronger Raman signals, a lower excitation wavelength would be appropriate. However, a shorter wavelength corresponds to a higher energy input and would increase the fluorescence. Other ways to increase the signals would be the use of higher laser powers and/or to extend the measurement time (integration time), but this would thermally destroy the samples and alter the resin spectra. Apart from this, both lower excitation wavelengths and higher laser powers pose a danger to the human eye. The use of such laser configurations in industrial plants is associated with many restrictions and makes the Raman method unattractive. In addition, it was found that the intended application requires comparatively long integration times, which is not suitable for fast sorting tasks. Therefore, it was decided to abandon this approach.

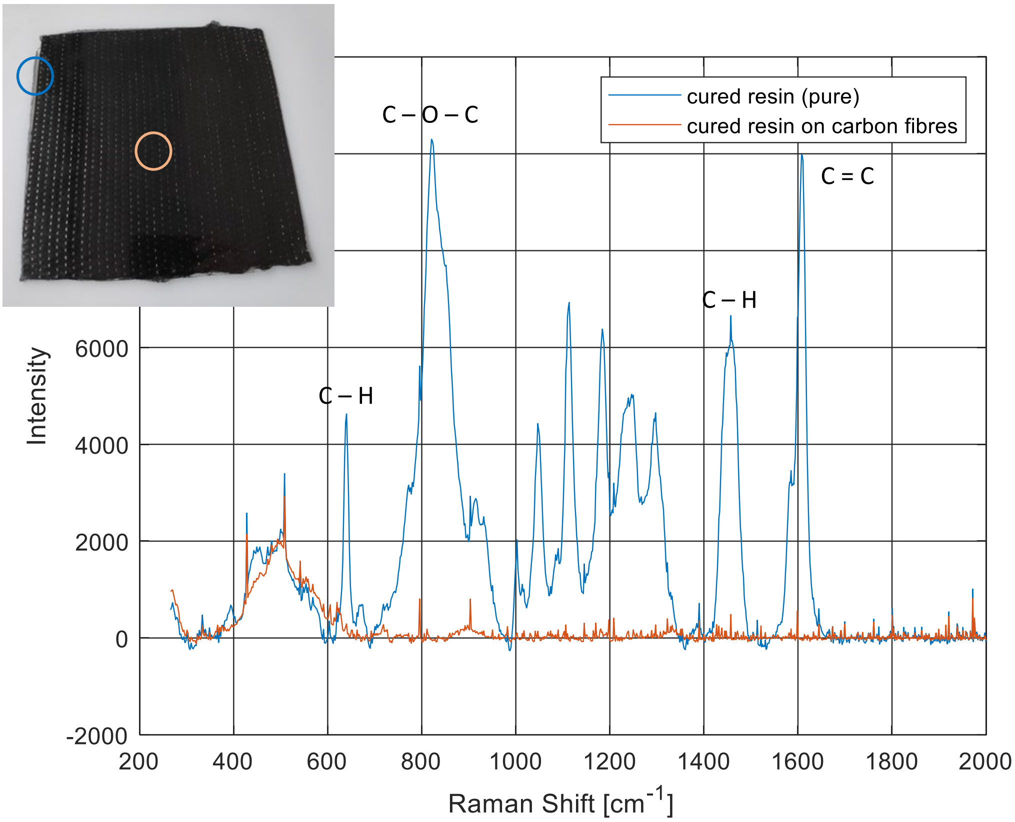

Figure 15. Baseline-corrected Raman spectra of a CFRP panel with amine-based epoxy resin system. While the peaks of the pure resin (blue) are clearly visible and can be identified with the help of the literature, the resin peaks collected on the fibres (red) are extremely weak and often cannot be distinguished from noise.

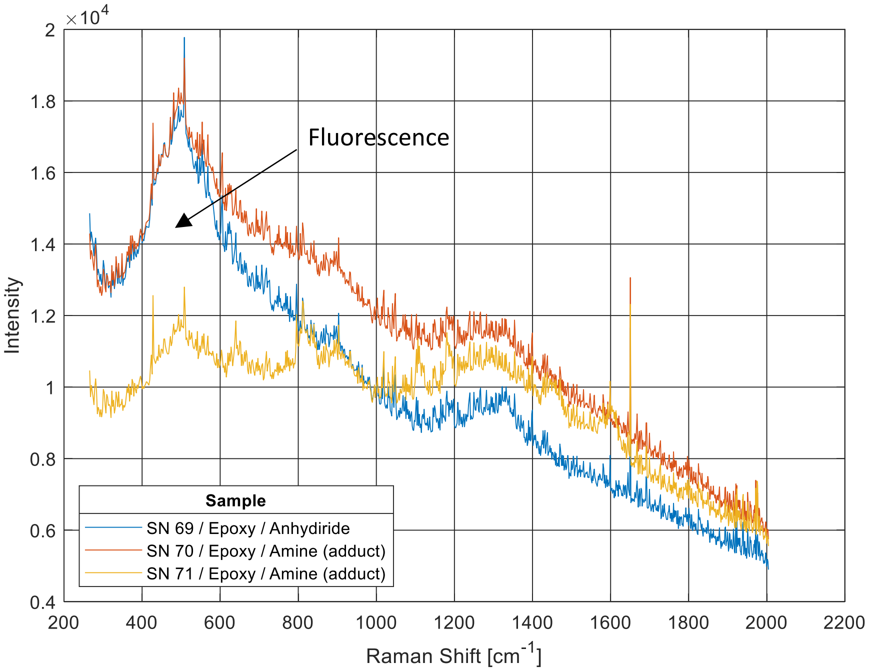

Figure 16. Raman spectra of CF samples with epoxy resin system that contain unspecific signals and a lot of noise. In addition, strong fluorescence is present.

4. SORTING OF CARBON FIBRE PARTS

Near-infrared (NIR) spectroscopy was found to be the most promising method for the non-destructive identification of the resin system of carbon fibre composites. In this section it will be discussed, how this method is actually employed for the automated classification of CF parts according to their resin system. As part of a sorting experiment, several carbon fibre samples made of amine-based epoxy resins have been measured one after the other using the NIR method, followed by the measurement of two samples made of epoxy anhydrides. To create a resin classification model, the recorded spectra were then subjected to a **partial least-squares discriminant analysis (PLS-DA)**. This classification method is used in chemometrics to analyse / 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 important sample features, e.g. membership of experimental groups. This explains, why the creation of a classification model requires reference materials with known composition.

The result of the PLS-DA is presented in Figure 17. It shows that the method is able to separate the two material classes (CF parts with epoxy amines and epoxy anhydrides) from each other. In principle, this classification model can now be applied in real time to new samples with unknown resin system. After each analysed sample, the corresponding classification result is forwarded to the control unit of a pneumatic sorting unit in the form of an electrical signal. The sorting unit then carries out the fractionation. For the application of this model in an industrial sorting plant, however, it is advisable (for statistical reasons) to include considerably more samples in the model, possibly even samples with other resin systems.

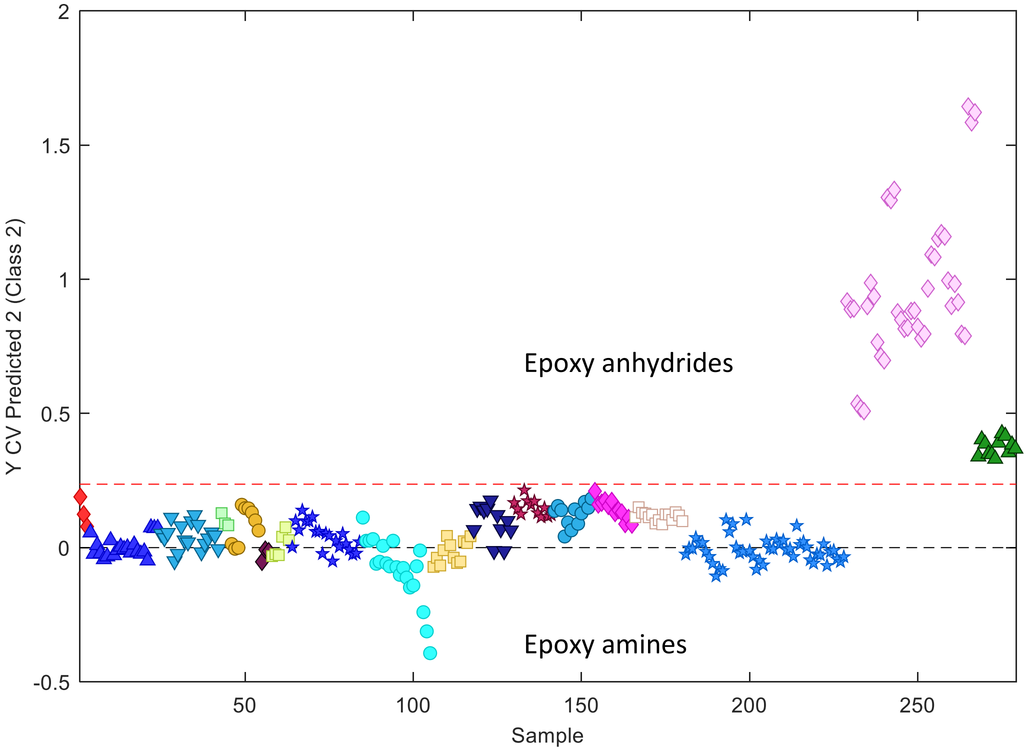

Figure 17. PLS-DA classification model for CF samples made of epoxy amines and epoxy anhydrides. While each individual symbol corresponds to a recorded spectrum, symbols of the same type and colour belong to the same CF sample. The dashed red line represents the ‘'detection threshold” and separates the two material classes from each other.

5. SUMMARY & CONCLUSIONS

The MC4 long-term circular approach for carbon fibre waste is to establish a chemical recycling process for cured waste and end-of life parts that causes minimal damage to the fibres and enables them to be re-used as yarns, rovings, mats and fabric through spinning and weaving processes. This chemical process is being developed by GAIKER within the project. It involves the separation of matrix (resin) and fibres and focuses on parts containing epoxy resins with amine hardeners.

To make sure no other resins, especially no epoxy anhydrides, enter into the chemical processing, the parts need to be sorted based on their chemical composition. As the basic requirement for mechanical sorting is a reliable material recognition, the task of i-RED was to develop a quick and non-destructive method that is able to do this job. Three different approaches, all of them based on molecular / vibrational spectroscopy, have been evaluated for this purpose: near-infrared (NIR) spectroscopy, mid-infrared (MIR) spectroscopy and Raman spectroscopy. The challenge was to obtain sufficient signal / information from the materials, as carbon fibres are black in colour and therefore reflect very little light.

The experimental results reveal that NIR spectroscopy is the most promising method for the identification of the resin system of carbon fibre composites, provided that an optimised refection optics with an elliptical reflector is used for illumination and signal collection. Using this setup, it could be shown that despite the low reflectivity of carbon fibre parts, sufficiently strong NIR signals are received from these materials. In addition, it was found that the NIR spectra of carbon fibre parts with epoxy amines have many features in common, which differ significantly from the features in the spectra received from parts containing epoxy anhydrides. This means that the requirements are met to clearly identify parts with epoxy amines and to distinguish them from parts with of epoxy anhydrides. The capability of a partial least-squares discriminant analysis (PLS-DA) has been demonstrated for the classification of carbon fibre composite parts in a sorting process.