

# FLUORESCENT MARKING OF FIBER REINFORCED POLYMER FOR COMPONENT AND MATERIAL IDENTIFICATION IN THE CONTEXT OF MATERIAL FLOW CANALIZATION

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**Abstract:** For a circular economy, the ability of a precise identification of products and materials in all life cycle phases is an enabler. Markers can be used effectively for material identification and they can also be physically integrated into the semi-finished polymer. This paper focuses on the integration of fluorescent particles into fiber-reinforced composites (FRC) via VARI infiltration. Initial experimental studies show possibilities for the application of markers in FRC. Thereby, interaction between marker particles, FRC and manufacturing process variations are analyzed. Additionally, the influence of textile permeability on the particle distribution of markers within the composite is addressed. When processing these polymer mixtures within a VARI process, the reinforcement textiles and processing aids lead to the filtration of marker particles, which is why process execution must be adapted to achieve a more efficient marking process.

**Keywords:** Tracer-Based-Sorting; fluorescent particles; continuous fiber reinforced polymers; thermoset polymers; VARI; marker technology

## 1. Introduction

For a functional and efficient circular economy, the ability to precisely identify products and materials in all life cycle phases is necessary. This is especially relevant for the End-of-Life phase where often no closed chain of information to identify products and materials for efficient reuse or recycling is available. For various product categories surface placed identification technologies are existing such as QR-codes or embossed labels. In addition to these technologies, material integrated solutions are emerging. One of these technologies is the integration of fluorescent particles into the material itself. These particles enable robust material and structure identification possibilities in all product life cycle phases for the realization of circular economies (cf. Figure 1).

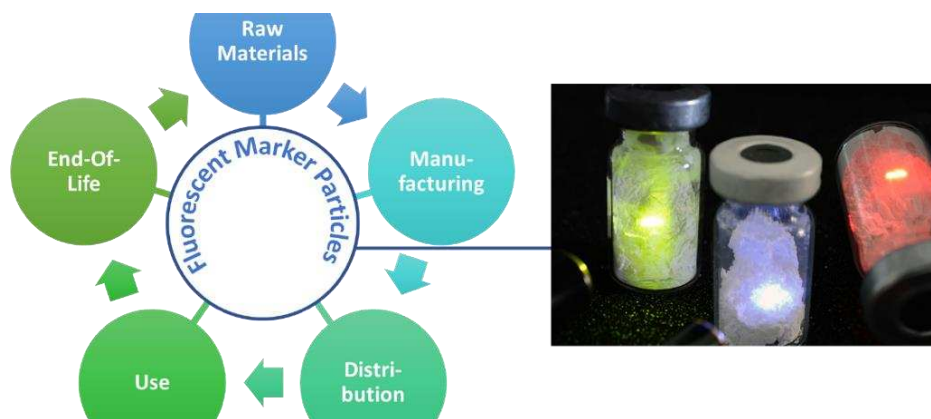


Figure 1: Fluorescent markers for material and structure identification in life-cycle phases

The market for glass fiber reinforced plastics (GFRP) and carbon fiber reinforced plastics (CFRP) is expected to grow significantly in the next years partly due to the rise in renewable energy activities [1]. While currently there is no widespread established universal recycling method for most of these materials, there is progress in research and development for different recycling technologies in this field [2]. Some of the problems faced are unknown material combinations and other contaminants in the composites. FRCs with continuous fiber reinforcement are expected to bring new challenges to the use of fluorescent particles compared to unfilled plastics, like optical absorption changes, refraction or inhomogeneous particle distribution due to filtration processes. Thus, the interaction between the markers, manufacturing parameters and reinforcement architecture has to be investigated.

As of now there are various research activities for the use of tracer-based-sorting in unfilled and short fiber reinforced thermoplastics for food packaging and window frames, where they show a high potential for enabling circular economy models [3]. Currently there is no research available for the integration of fluorescent particles into fiber reinforced plastics (FRP) with continuous fibers such as CFRP or GFRP.

## **2. Fluorescent marker technologies for individual product identification**

The fluorescent marker particles used in this paper are crystals with a grain size of more than 1  $\mu\text{m}$ . They glow in a characteristic color when excited with near infrared light. Consequently, the fluorescent particles are invisible in ambient light. In addition, the fluorescent particles are thermally and chemically stable and exhibit low solubility behavior. They show good biocompatibility with unobjectionable toxicological test results and are compliant with EU substance law requirements. Due to these properties, fluorescent particles can easily be integrated as an additive in polymeric materials and can be processed in existing production processes. Currently, two distinct technologies that use fluorescent particles are tracer-based-sorting and particle fingerprints.

Tracer Bases Sorting (TBS) opens the possibility of sorting according to arbitrarily definable criteria. It is independent of material properties, robust against deformation and contamination and can be used flexibly. Currently TBS relies on three markers with different spectral properties. To enable identification of more than three different categories, the three markers are mixed in predefined ratios. For example, a 20 % gradation of ratios can generate 21 marker codes. The particles (tracers) can be inserted into the material or applied to the product e.g., by printing or using labels. By mixing the tracers into the material, every part of the material get its own traceable information.

Currently, neat polymers are well detectable by e.g. near infrared sorters and thus subsequently sorted. As this differentiation is usually not sufficient, TBS can be used as an additional decision criterion or as a standalone solution. For example, TBS can be used to separate composites from non-composites. These have the same main polymer on the surface and would thus fall into the same category of NIR sorting. One of the main advantages of material integrated traces for TBS is the robustness against wear and destruction, which enables identification of already crushed material, which is especially beneficial in the recycling industry.

Particle Fingerprints is a technology to apply a unique marking into a product, that is forgery-proof and that can be used to link the product to a database entry e.g., a digital product pass. The technology is based on identification of the geometric distribution of fluorescent particles

(markers), which have been added to the raw material (e.g. plastic, ceramic, metal or coatings) in advance and thus are arranged in a completely random manner within the production process. Due to the aspect of randomness, the resulting "fingerprint" cannot be copied or reproduced. In contrast, barcodes, RFID tags or digital watermarks are produced by deterministic processes. There is a kind of recipe according to which the codes are produced, which makes it possible to forge and replicate them. The PFP, on the other hand, is unique. Consequently, its use for product identification and authentication is particularly suitable for security and health-related objects and for products that are heavily affected by counterfeiting.

The PFP is particularly suitable for mapping digital product passports because of its high level of protection against forgery and manipulation due to the role of randomization. This also means that an almost infinite number of different fingerprints can be generated.

The main difference between PFP and TBS is that PFP considers the spatial distribution of the markers, while TBS detects the spectral properties of the markers, which is shown in Figure 2. For the best results of these technologies, PFP uses larger particles with a diameter between 30  $\mu\text{m}$  and 50  $\mu\text{m}$  compared to TBS with particle diameters from 5  $\mu\text{m}$  to 10  $\mu\text{m}$ .

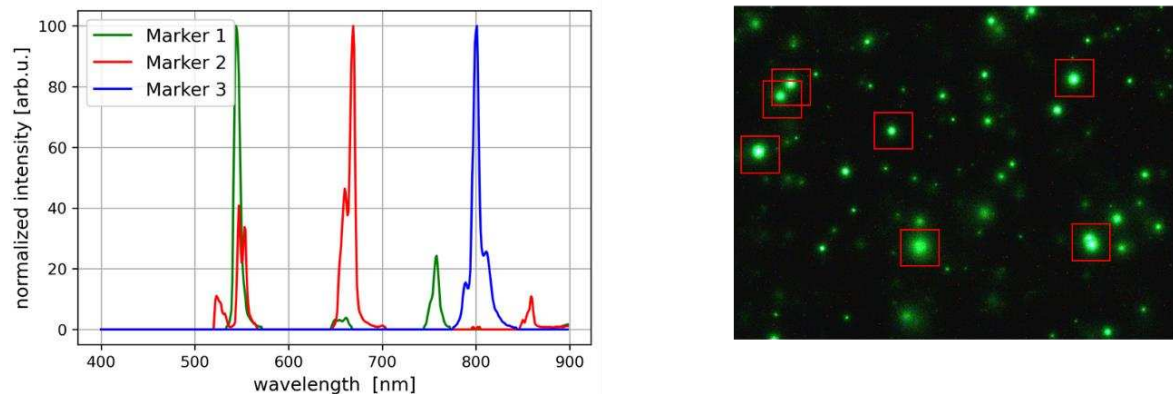


Figure 2: Identification of different TBS markers by spectral analysis (left) and a PFP by spatial distribution analysis (right)

### 3. Experiments on feasibility of marker integration into continuous fiber reinforced thermosets via vacuum assisted resin infusion

Figure 3 shows the Vacuum Resin Infusion (VARI) process setup to investigate the processability of marker filled resin systems. The main advantages of using the VARI process are, that it enables fast and cost-efficient manufacturing of test specimens due to simple tooling, whilst still providing conclusions on preform related filtration effects for other infusion and injection processes as well as being a relevant manufacturing process for high performance structures.

The preform consists of a layup of 10 layers of unidirectional glass or carbon fiber textiles, which are placed with the same orientation upon a solid glass ground plate.

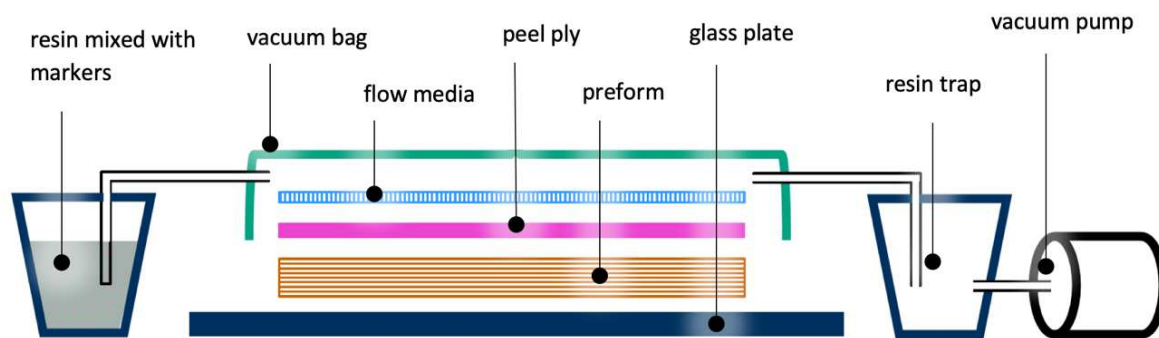


Figure 3: VARI process setup for marker infiltration

A peel ply is placed on top of the preform to ensure a damage free demolding of the FRP after curing. Due to low permeability of the unidirectional textiles, a flow media is used on top of the peel ply, to allow a homogenous resin infusion over the whole textile surface. The layup is covered by a vacuum bag, which is sealed against the glass plate. Vacuum is applied via an outlet tube that connects to a resin trap and vacuum pump. The resin is infiltrated via vacuum through the inlet tube on the other side that connects to a container filled with epoxy resin. The fluorescent particles will be mixed into the resin prior to the infusion.

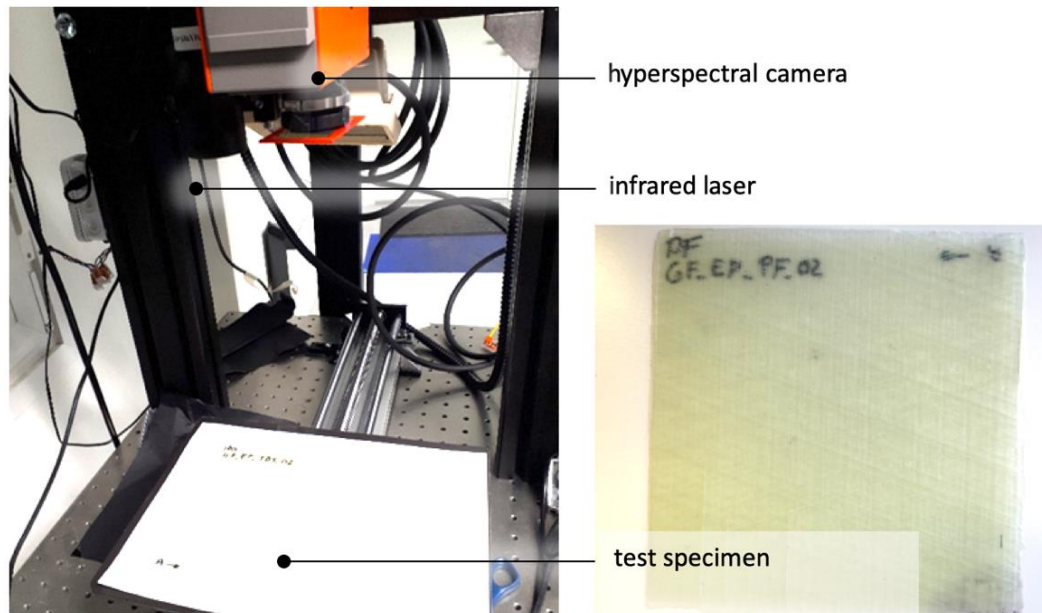
In the investigations, four combinations of fluorescent particles and preforms are examined, which are shown in Table 1. Thereby, GF-TBS means glass fiber textiles using TBS-technology, CF-TBS means carbon fiber textiles and TBS technology. In case of GF-PFP glass fiber textiles were used in combination with PFP marking technology.

Table 1: Overview of test specimens

ID number	Fiber Type	Textile weight	Textile ply thickness	Marker type
GF-TBS	Glass fiber	250g/m <sup>2</sup>	0.2 mm	TBS
GF-PFP	Glass fiber	250g/m <sup>2</sup>	0.2 mm	PFP
CF-TBS	Carbon fiber	200g/m <sup>2</sup>	0.2 mm	TBS

For all test specimens the same resin (Epoxy L) and curing agent (W300) is used. A total combined weight of 300 g is mixed according to the manufacturer recommended ratio. For all marker types a particle concentration of 300 ppm is chosen, which results in a mass of 0.06 g of marker particles. The particles were mixed homogeneously into the resin before infusion. After infusion, the resin is cured under room temperature.

For evaluating the marker concentration and distribution in the final FRP, the specimens were analyzed using a hyperspectral camera. Therefore, an infrared laser is used for the excitation of the fluorescent particles within the FRP samples. The used setup is shown in Figure 4. Purely optically, the marker particles are not visible in the manufactured test specimen.



*Figure 4: Test setup for the determination of the marker concentration (left) and visual impression of FRP specimen (right)*

For all further results, the specimens were excited by laser light showing a wavelength of 980 nm. Additionally, for all specimens the light intensity of the fluorescent particles is measured for the wavelength of 550 nm. To enable the comparison between different specimens all intensities are normalized to the highest measured intensity of the first test specimen.

#### **4. Interpretation of the results**

First, the feasibility of mixing the particles into the resin have been analyzed. Therefore, the particles are mixed into the resin using a conventional stirrer. By using an infrared laser pointer with a wavelength of 980 nm, the distribution within the resin can be easily visualized. For both marker types no agglomerations could be identified. Furthermore, since the particle concentration is low, there is no measurable impact to the resin properties, such as viscosity. Thus, the infusion process itself will not be influenced not by the integration of marker particles with these concentrations. This is also shown by the finished FRP specimens, that show no visible quality differences to their counterparts without integrated marker particles.

Afterwards the resulting concentration and distribution of marker particles within the FRPs is analyzed. Figure 5 shows the normalized light intensity at a wavelength of 550 nm for the fluorescent markers with the hyperspectral camera tests for GF-TBS on the tool and non-tool side. Tool side referring to the side oriented towards the glass plate during infiltration.

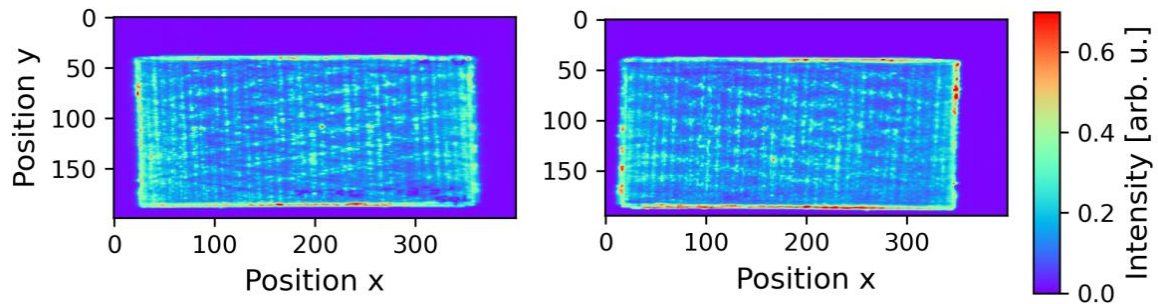


Figure 5: GF-TBS – normalized light intensity at 550 nm wavelength on the tool side (left) and non-tool side (right)

The test setup is not able to measure exact length measurements, which is why the visual results are morphed and not in proper scale. The test specimen orientation can be seen in Figure 6 for comparison. This orientation is true for all further hyperspectral camera results. The TBS marker particles can clearly be identified from both specimen sides. Further analysis shows, that the particles are only situated on the non-tool side of the specimen. This means due to low permeability of the textiles all particles are filtered through it and don't infiltrate through to the tool side. Due to the transparent properties of the glass fibers and thermoset matrix, the particles can still easily be identified on the tool side.

Figure 6 shows normalized intensity results of the fluorescent markers with the hyperspectral camera tests for GF-PFP.

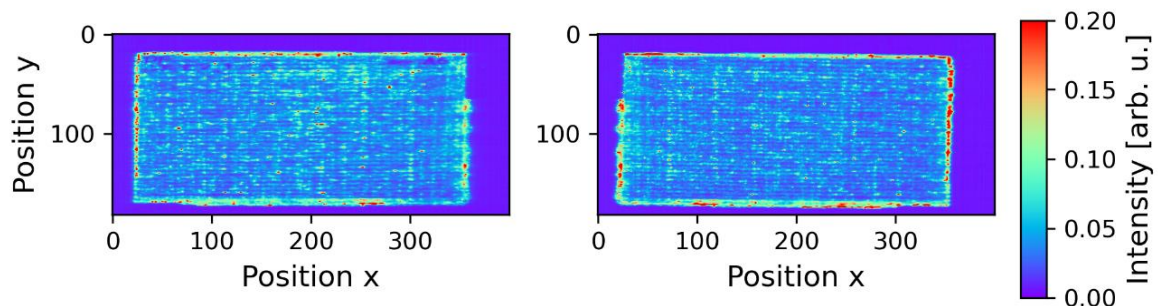
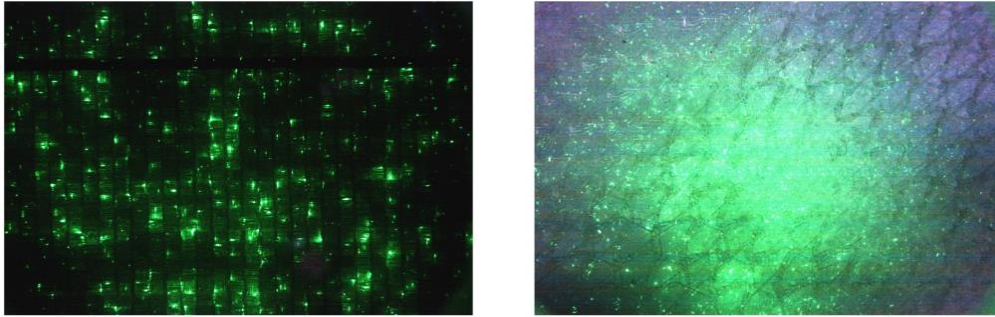


Figure 6: GF-PFP - normalized light intensity at 550 nm wavelength on the tool side (left) and non-tool side (right)

For PFP the particles can also clearly be identified through both sides, however the intensity is lower compared to TBS. This can be a result due to less PFP particle mass in the specimen as well as the larger size of the PFP particles compared to TBS, which can result in a lower luminescence intensity as a certain mass of bigger particles has lower intensity as the same mass of smaller particles due to volume effects.

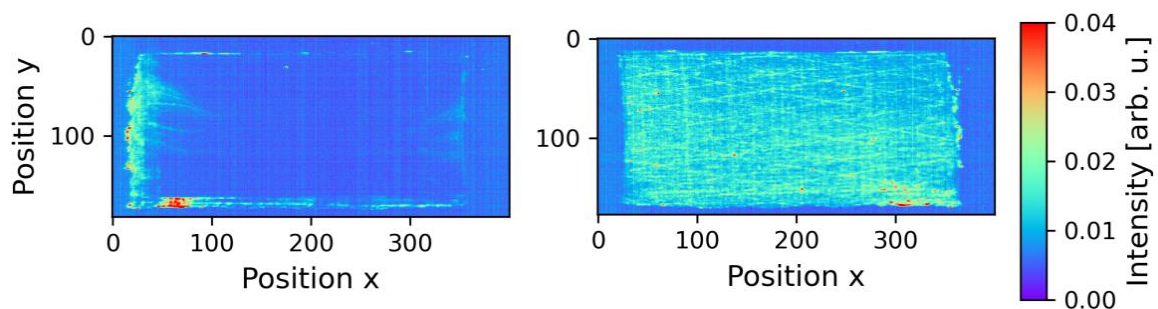
Looking at the peel ply and flow media through a PFP detection camera setup, it is apparent, that these aids filter the larger PFP particles, which can be seen in Figure 7.



*Figure 7: Distribution of the marker particles: PFP particles (green) filtered in the peel ply (left) and the flow media (right)*

Thus, the lower intensity for the PFP specimens is caused by the filtration and thus a lower particle concentration in the FRP.

Furthermore, the influence of the substitution of glass fiber with carbon fiber textiles is analyzed. Figure 8 shows the hyperspectral camera results for the CF-TBS specimens.



*Figure 8: CF-TBS- normalized light intensity at 550 nm wavelength on the tool side (left) and non-tool side (right)*

Looking at the tool side, the filtration effect of the textile layup is clearly shown. Particles only overflow on the sides but an infiltration through the textiles is not detectable. Since the carbon fibers are not transparent, identification through the textile layup is not easily possible. The normalized intensity of TBS particles on the top side is significantly lower for CF-TBS compared to GF-TBS. This is due to higher light absorption of carbon fibers which results in their black color.

## 5. Conclusions

Within this paper methods and experimental investigations for the traceability of FRP during the whole life cycle considering circular economy are presented. The investigations show that the integration of fluorescent markers into FRPs during manufacturing via VARI process is possible. The markers can be homogeneously mixed into the resin and show no significant impact on process parameters for the resin, thus having no direct influence on the infusion process. For both TBS and PFP the textile layups of unidirectional plies show a significant filtration effect resulting in insufficient particle concentrations on the tool side of the FRP specimens. For transparent or translucent fiber/matrix combinations this is a minor problem since the particles can still be identified via both sides of the FRP plates. For non-transparent fiber/ matrix

combinations, such as CFRP, the markers can only be identified from the non-tool side of the specimen.

Due to larger particle size, the use of PFP within the VARI process is prone to filtration effects by process aids, such as peel plies and flow media. Therefore, the standard VARI process setup is not ideal for the use of PFP technology. Possible solutions for the integration of PFP technology could be PFP labels, which then will be integrated on top of the preform during infusion.

The integration of TBS particles into transparent FRPs using the VARI process seems promising, but further research with regard to optimizing process parameters must be conducted. The integration of TBS particles into FRPs with high optical absorption, like carbon fiber reinforced composites results in poor detectability of the particles. A possible solution could be the integration of top layers with low absorption on top of the carbon fiber plies, which could improve the detectability.

## **6. Acknowledgement**

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