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

# Deliverable D3.6: “Liquid recycled fraction for amine epoxy resin”

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Profactor

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| **Dissemination Level** | | |
| **PU** | Public | X |
| **SEN** | Sensitive information | |

# Contents

# 1. OBJECTIVES

The main objectives of this deliverable, "D3.6 - Liquid recycled fraction for amine epoxy resin," are to demonstrate and analyse the influence of incorporating different fractions of chemical products obtained during the solvolysis process of cured waste carbon fibre reinforced plastics. This solvolysis process was developed by GAIKER as part of the deliverable "D3.4 - Recycling process for cured parts." The process products, specifically the organic fractions generated during solvolysis, were further characterized and evaluated in "D3.5 - Feasibility study on vitrimerization."

The current deliverable is organized into several key sections to provide a comprehensive understanding of the work conducted. Initially, a detailed explanation is provided on the chemical solvolysis process, including its stages and the methods used for collecting the chemical products formed during the solvolysis reaction. This section outlines in general the underlying mechanisms of the process and the significance of the resulting liquid fractions as potential components for resin systems.

Following this, the methodology for incorporating the recovered chemical products into the resin formulations is described. Resin samples were fabricated at NOMA using NOMA's amine-based resin system. The quality of these fabricated resin samples was evaluated through a series of mechanical and material characterization tests to assess their performance and compatibility with the recycled liquid fractions.

In the subsequent sections, the document presents the results of bending tests conducted on the fabricated resin samples. These tests provide critical insights into the mechanical properties, such as strength and flexibility, of the modified resins. Additionally, the deliverable includes detailed observations from Scanning Electron Microscopy (SEM) analyses, which were carried out to examine the microstructure and morphology of the samples produced through the casting process. These microscopic observations are essential for understanding the interaction between the recycled fractions and the amine-based epoxy matrix, as well as identifying potential defects or enhancements in the material structure.

# 2. METHODOLOGY

In this section, stages of the solvolysis process, where liquid fractions were obtained for the tests to check their compatibility with NOMA epoxy resin, are shown. Further, equipment, synthesis methodology, as well as selected cores with different functional groups and their characteristics, are presented.

## *2.1 Stages of solvolysis process*

Detailed chemical stages of solvolysis process were described by GAIKER in D3.4, see Fig. 1. In general, organic fractions for fabrication of the composites, presented in Section 3 of the deliverable, were obtained during different stages of the developed solvolysis process. The process was applied to cured carbon fibre reinforced plastics waste and included chemical preparation such as neutralization, evaporation and separation of phases subjected for further processing. Six different organic fractions were separated namely: neutralized fraction (NF), organic phase (1st extraction) (OP1), organic phase (2nd extraction) (OP2), aqueous phase (2nd extraction) (AP2), solid fraction recovered (SF) and liquid fraction recovered (LF). Chemical compositions of fractions were characterized in D3.5 by CEA.

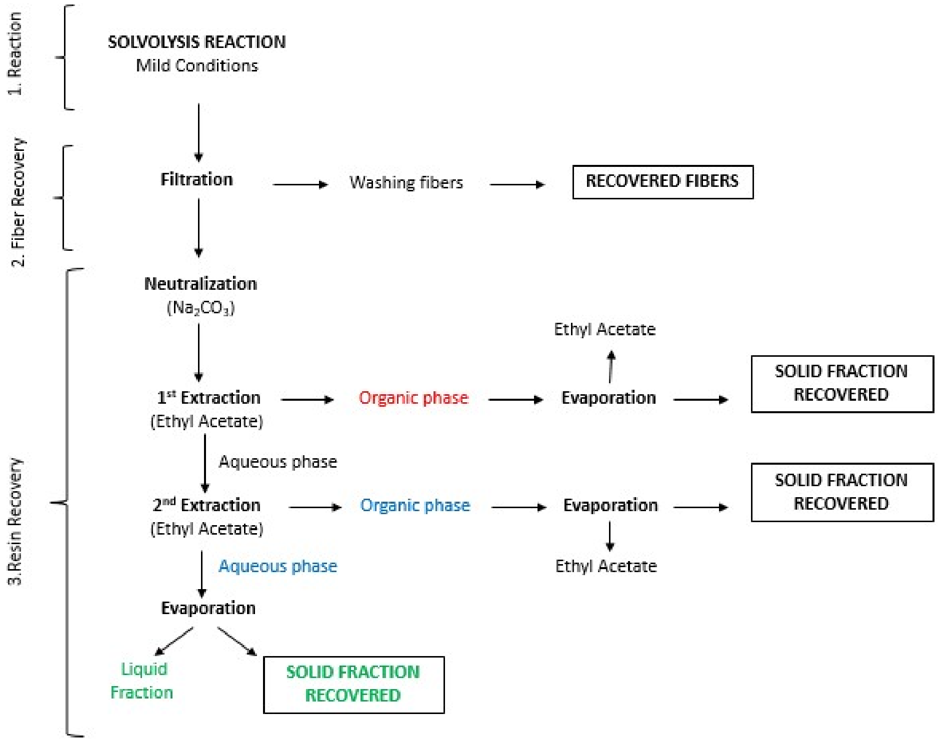

*Fig. 1: Scheme of solvolysis process steps developed by GAIKER with indicated stages for different phases separation.*

## 2.2 Samples fabrication methodology

### 2.2.1 Delivered samples without neutralization- aeronal waste (AW)

The detailed chemical stages of the solvolysis process showed in Fig. 1 were described by GAIKER in deliverable D3.4. In general, the organic fractions used for the fabrication of composites, as presented in Section 3 of the deliverable, were obtained during various stages of the developed solvolysis process applied to waste cured carbon fibre-reinforced plastics (CFRPs). The process involved multiple chemical preparation steps, including neutralization, evaporation, and phase separation, to isolate materials for further processing.

Aeronal waste sample (AW)

Solution of
AW in NOMA
HV resin

Epoxy/AW specimens for
mechanical testing

*Fig. 2: Typical stages of samples preparation based on solvolysis liquid fractions before neutralization*

Six distinct organic fractions were successfully separated during the solvolysis process: the neutralized fraction (NF), organic phase from the first extraction (OP1), organic phase from the second extraction (OP2), aqueous phase from the second extraction (AP2), solid fraction recovered (SF), and liquid fraction recovered (LF). Each fraction corresponds to a specific stage in the solvolysis process and possesses unique chemical properties that determine its suitability for further use in composite development.

The chemical compositions of these fractions were thoroughly characterized and documented in deliverable D3.5 by CEA, providing essential insights into their structural properties. These results highlight the effectiveness of the solvolysis process in breaking down cured CFRP waste into reusable components. By recovering both organic and solid fractions, this approach supports the development of sustainable composite systems and contributes to the principles of a circular economy, minimizing environmental impact and promoting material reuse.

The prepared mixture, containing 1 wt.% of aeronal waste (AW), was poured into pre-prepared moulds designed for the fabrication of specimens used in mechanical testing. The curing process was performed in two stages: the first stage involved curing at room temperature (20 °C) for 24 hours, followed by a second stage of post-curing at an elevated temperature of 60 °C for 6 hours. This two-step curing process ensured complete cross-linking of the epoxy matrix and improved the mechanical properties of the final material.

Once the curing process was completed, the specimens were demoulded and prepared for mechanical testing according to the appropriate standards to ensure consistency and accuracy in the evaluation of the resin system containing dissolved AW.

### 2.2.2 Delivered samples after neutralization- neutralized waste (NW)

The second type of samples obtained by GAIKER - neutralized waste (NW) were dissolved in acetone to remove residues after the neutralization process (Fig. 3). Samples after solvolysis were treated with acetone at room temperature, using a mechanical stirrer for 1 h. After filtration on a filter, the precipitate was dried and implemented in epoxy resin. After mixing with the LV/MR epoxy system (100:30 w/w), samples were cured for 24 h at room temperature (20 °C), then 6 h at 60 °C. The amount of NW in the resin system was 1 wt.%.

Neutralized waste sample (NW)

Acetone solution of NW

Filtration of NW

Sample after acetone treatment

Epoxy/NW specimens prepared for mechanical testing

*Fig. 3: Typical stages of samples preparation based on solvolysis liquid fractions after neutralization*

## 2.3 Resin characteristics

The mechanical properties and processing parameters of NOMA resins (*part per hundred of resin; **100 g of mixture measured at 23 °C) used in processing of liquid solvolysis fractions are listed below.

| MECHANICALPARAMETERS | | | | | |
|---|---|---|---|---|---|
| PARAMETER | UNIT | SYSTEM | | | STD. |
| | | ULV/HRLV/HR MV/HR | ULV/MR LV/MR MV/MR | ULV/LRLV/LR MV/LR | |
| Density | g/cm$^3$ | 1.14<br>1.18<br>1.17 | 1.14<br>1.16<br>1.15 | 1.14<br>1.11<br>1.12 | ISO 1183 |
| Impact strength | kJ/m$^2$ | 90<br>77<br>89 | 82<br>78<br>77 | 81<br>90<br>88 | ISO 179 |
| HDT | °C | 81<br>77<br>78 | 82<br>80<br>80 | 82<br>77<br>78 | ISO 75A |
| Tensile strength | MPa | 83<br>79<br>88 | 87<br>80<br>77 | 85<br>85<br>84 | ISO 527-2 |
| Young modulus | GPa | 3.3<br>3.1<br>2.9 | 3.2<br>3.0<br>3.0 | 2.8<br>3.0<br>2.9 | ISO 527-2 |
| Flexural strength | MPa | 119<br>122<br>125 | 128<br>130<br>134 | 124<br>128<br>125 | ISO 178 |
| Flexural modulus | GPa | 3.1<br>3.2<br>3.1 | 3.2<br>3.3<br>3.3 | 3.3<br>3.2<br>3.2 | ISO 178 |
| Elongation at break | % | 7.0 | 8.0 | 6.8 | ISO 527-2 |
| Compressive strength | N/mm$^2$ | > 100 | > 100 | > 100 | ISO 604 |
| Absorption of water after 7 days | % | < 0.5 | < 0.5 | < 0.5 | ISO 175 |

*Table 1: Mechanical properties*

| PROCESSING PARAMETERS | | | | | | | |
|---|---|---|---|---|---|---|---|
| PARAMETER | UNIT | RESIN (A) | | | HARDENER (B) | | |
| | | ULV | LV | MV | HR | MR | LR |
| Viscosity (at 23 °C) | mPa s | 300-350 | 500-600 | 1,200-1,600 | < 20 | < 20 | < 20 |
| Density (at 23 °C) | g/cm$^3$ | 1.05 | 1.11 | 1.20 | 0.95 | 0.92 | 0.92 |
| Mixing ratio | phr* | | 100 | | 30 | 28 | 31 |
| | | | | | Mixture | | |
| Pot-life** | approx. in min | | | | 30 | 60 | 120 |

**part per hundred of resin; **100 g of mixture measured at 23 °C*

*Table 2: Parameters for processing of NOMA resins.*

## 2.4 Methods and equipment for sample characterization

**Three-point bending:**
To evaluate the effect of the chemical modifications of the epoxy resin and rCF on flexural strength and flexural modulus of elasticity, a static three-point bending test was carried out based on ASTM D7265 standard. Both the support rollers and the load roller had a diameter of 3 mm, and the displacement speed of the beam was 1 mm/min. The specimens were 80 × 13 mm in size, while the support spacing was 16 times the thickness of the tested composites. This test was carried out on an MTS QTest10 testing machine, equipped with a 10 kN force sensor. Based on the determined courses of stress change as a function of strain, the flexural strength and the flexural modulus of elasticity Ef chord were determined, which are described by the following equations:

Flexural strength: $\sigma_f = \frac{3PL}{2bh^2}$

(where: P - maximum force; L - support spacing; b - specimen width; h - specimen thickness)

Flexural modulus of elasticity Ef chord: ${E_f}^{chord} = \Delta\sigma/\Delta\varepsilon$

(where: Δσ - change in bending stress between two selected strain points (1,000 and 3,000 με); Δε - difference between selected strain points (2,000 με))

**Tensile strength:**
The tensile strength and Young's modulus of epoxy-based resins were determined through a tensile test, conducted according to ISO 527 standard. The material’s mechanical properties under tension were evaluated, providing insights into its structural performance in the result of application of different kinds and concentration of liquid fractions obtained from the solvolysis process. Standard test specimens, 80 × 10 × 4 mm, were used. The specimens were conditioned at 23 °C ± 2 °C and 50 % relative humidity for 24 h to ensure consistent results. The tensile test was performed using a universal testing machine equipped with grips to hold the specimen securely. Extensometers were attached to measure elongation accurately. During the test, a uniaxial tensile load was applied at a constant crosshead speed, i.e., 1 mm/min, depending on the standard. As the load was increased, the applied force and the corresponding elongation were recorded by the machine. This data was used to generate a stress-strain curve, which characterized the material's behaviour under tension. Tensile strength was calculated as the maximum stress the material could withstand before fracture, obtained by dividing the maximum applied force by the initial cross-sectional area of the specimen. Young's modulus was derived from the slope of the linear (elastic) portion of the stress-strain curve. It represented the ratio of stress to strain within this elastic region, indicating the material’s stiffness.

**Heat deflection temperature (HDT):**
The Heat Deflection Temperature (HDT) test measures the temperature at which an epoxy-based material deforms under a specified load. This is essential for understanding the material’s thermal performance. Tests were performed according to ISO 75 standard, the process begins with specimen preparation. Standard rectangular specimens, 80 × 10 × 4 mm (ISO), were conditioned at 23 °C ± 2 °C and 50 % relative humidity for 24 h. The test apparatus consists of a heating bath (oil or air), a deflection measurement device, and weights to apply a constant load. In a three-point bending setup, the specimen is placed on two supports with a span of 100 mm, and a load is applied to create a specified stress level—to 1.82 MPa. The bath temperature started from room temperature and increases at a controlled rate of 2 °C/min. Throughout the test, deflection was continuously measured, and the temperature at which the specimen deflects 0.25 mm was recorded as the HDT.

**Scanning Electron Microscopy (SEM):**

The microstructure of composites was investigated using a scanning electron microscope (SEM) SEM TM3000 from Hitachi. The microsection was prepared using conductive resin and grinding and polishing of the specimen. Samples were coated with gold/palladium mix using POLARON SC7640 from Quorum Technologies Ltd (parameters: 90 s, 10 mA, 1.5 kV). Images were taken with an accelerating voltage of 5-15 kV. Polished cross sections of the manufactured composites were observed.

# 3. RESULTS

## 3.1 Mechanical and thermal properties

All fabricated samples containing organic fractions were subjected to mechanical and thermal property investigations. The results for the aeronal waste (AW) and neutralized waste (NW) at concentrations of 1 wt.% and 2.8 wt.%, respectively, are summarized in Table 3. The organic fractions were mixed with NOMA HV/MR resin to evaluate their impact on material properties.

As shown in Table 4, the addition of organic fractions, both aeronal waste (AW) and neutralized waste (NW), had a noticeable effect on the samples' mechanical properties. From the perspective of flexural strength, the sample labelled NOMA HV/MR/NW (containing neutralized waste) exhibited the smallest decrease compared to the reference sample. However, while flexural strength was relatively better preserved, the tensile strength and heat deflection temperature (HDT) of this sample were significantly lower than those of the reference material.

On the other hand, samples containing aeronal waste (AW) displayed the poorest mechanical properties overall. In all cases, the addition of AW led to a drop of more than 50% in flexural strength values compared to the reference sample. This severe reduction in mechanical performance made further testing of these samples unnecessary, and they were subsequently rejected.

These findings highlight that the type of organic fraction plays a crucial role in determining the mechanical behavior of the composite materials. While neutralized waste (NW) demonstrated slightly better compatibility with the NOMA HV/MR resin, the observed decreases in tensile strength and HDT indicate that further optimization is required to achieve acceptable performance levels. In contrast, the poor results obtained for aeronal waste (AW) suggest that it is not suitable for use in such resin systems without significant modifications or additional processing.

| Sample | Flexural strength [MPa] | Flexural modulus [GPa] | Elongation at break [%] | Tensile strength [MPa] | Young modulus [GPa] | HDT [°C] |
|---|---|---|---|---|---|---|
| Noma HV/MR (REF) | 107 | 2.8 | 6.5 | 88 | 3.2 | 71 |
| Noma HV/MR/AW | 37 | 2.2 | 5.0 | 61 | 2.0 | 70 |
| Noma HV/MR/AWR1 | 45 | 2.8 | 5.1 | 72 | 2.4 | 68 |
| Noma HV/MR/AWR2 | 41 | 2.6 | 5.4 | 75 | 2.5 | 68 |
| Noma HV/MR/NW | 96 | 2.5 | 5.0 | 71 | 2.7 | 65 |
| Noma HV/MR/RV1 | 80 | 2.4 | 5.2 | 76 | 3.0 | 71 |
| Noma HV/MR/RV2 | 71 | 2.3 | 5.0 | 74 | 3.1 | 71 |

Table 1: *Mechanical and thermal (HDT) properties for organic fractions mixed with NOMA resins.*

Further tests were conducted with three different concentrations for each separated organic fraction. Also in this case, similar to previous investigations, mechanical tests after bending and tensile strength tests as well as HDT investigations were conducted (Table 2).

For each organic fraction, optimal concentrations were selected from the point of view of obtained properties in comparison to reference samples without addition of any organic fractions. In the case of the organic fraction marked as NF, the optimal content in this case is 5 wt.%. These amounts did not lead to a decrease of bending properties, while tensile strength properties stay on reasonable level. In the case of the other fractions, in most cases also 5 wt.% was selected as the most efficient to sustain the properties from the reference sample. In some cases, an addition of 1 wt.% gave even better values in comparison to reference samples (OP2, SF, LF), but taking into consideration reasonable higher content of organic fraction which we can use, higher weight content was selected instead of little higher samples properties.

| Sample | Content of sample in epoxies [wt.%] | Flexural strength [MPa] | Flexural modulus [GPa] | Elongation at break [%] | Tensile strength [MPa] | Young modulus [GPa] | HDT [°C] |
|---|---|---|---|---|---|---|---|
| Noma HV/LRA (REF) | 0 | **93** | **3,1** | **2,9** | **69** | **3,0** | **71** |
| Noma HV/LRA/NF | 1 | 114 | 3,1 | 4,3 | 46 | 2,9 | 71 |
| | **5** | **98** | **2,6** | **5,0** | **56** | **2,5** | **72** |
| | 10 | 77 | 2,3 | 6,0 | 49 | 2,2 | 73 |
| Noma HV/LRA/OP1 | 1 | 103 | 3,2 | 3,2 | 40 | 3,0 | 71 |
| | **5** | **112** | **3,0** | **4,2** | **47** | **3,0** | **69** |
| | 10 | 71 | 2,6 | 7,0 | 39 | 2,5 | 51 |
| Noma HV/LRA/OP2 | 1 | 105 | 3,1 | 3,4 | 36 | 3,0 | 70 |
| | **5** | **102** | **3,0** | **7,9** | **36** | **2,8** | **65** |
| | 10 | 67 | 2,5 | 5,4 | 51 | 2,3 | 51 |
| Noma HV/LRA/AP2 | 1 | 112 | 3,1 | 4,0 | 59 | 2,9 | 72 |
| | **5** | **103** | **2,7** | **4,1** | **32** | **2,0** | **73** |
| | 10 | 59 | 2,0 | 4,0 | 26 | 1,9 | 71 |
| Noma HV/LRA/SF | **1** | **106** | **2,7** | **4,4** | **52** | **2,9** | **73** |
| | 5 | 66 | 3,0 | 2,3 | 45 | 2,9 | 73 |
| | 10 | 62 | 3,3 | 2,2 | 49 | 3,1 | 73 |
| Noma HV/LRA/LF | 1 | 114 | 3,1 | 4,0 | 58 | 2,8 | 73 |
| | **5** | **102** | **2,8** | **3,8** | **61** | **2,6** | **73** |
| | 10 | 55 | 2,0 | 4,0 | 23 | 1,8 | 72 |

*Table 2: Mechanical and thermal (HDT) properties for organic fractions mixed with NOMA resins.*

## *3.1 Microstructure of fabricated samples (SEM)*

Selected epoxy resin samples containing different organic fraction samples were analysed using scanning electron microscopy (SEM). They were prepared by polishing the cross sections of the samples and coated with a conductive layer and then investigated by means of microscopy.

Six different organic fractions were mixed with amine epoxy resin in three different concentrations, namely: 1) neutralized fraction (NF); 2) organic phase (1st extraction) (OP1); 3) organic phase (2nd extraction) (OP2); 4) aqueous phase (2nd extraction) (AP2); 5) solid fraction recovered (SF); 6) liquid fraction recovered (LF). Observations were conducted to investigate their microstructure with special attention to porosity which could indicate not enough compatibility between epoxy matrix and fractions obtained from solvolysis process or problems during degassing resulting in porosity. Based on the previously conducted mechanical tests, the most promising samples which at the highest level retained their mechanical properties were subjected for observations. From the mechanical properties point of view, the second criterion was to select mixtures with the highest concentration of the tested fractions with possible the lowest influence on the samples microstructure.

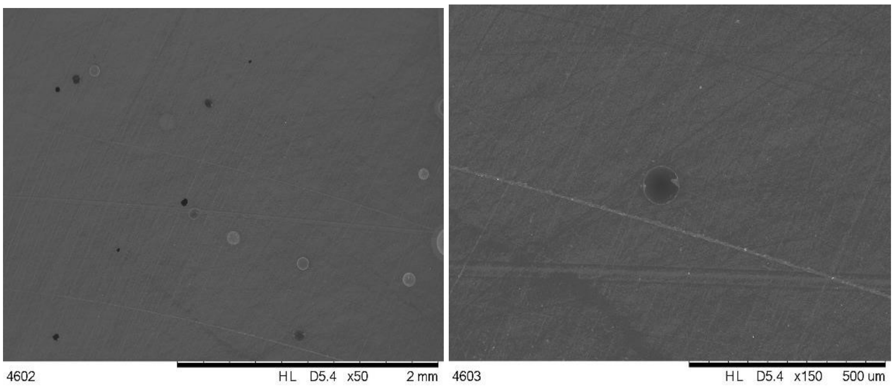

*Fig. 4: Samples containing 5 % of neutralized fraction (NF)*

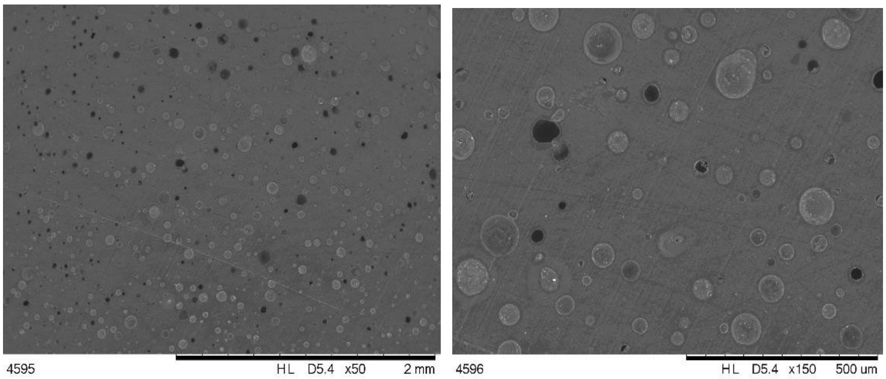

*Fig. 5: Samples containing 10 % of neutralized fraction (NF)*

As it can be seen in Fig. 4 and Fig. 5, the neutralized fraction samples at 5 wt.% revealed a small number of pores, whereas the 10 wt.% sample was characterized by a significantly porous structure. The size of the pores ranged from c.a. 50 µm up to c.a. 100 µm. Such high concentration of pores will negatively influence mechanical performance of the samples, thus in this case 5 wt.% concentration was found as the most optimized.

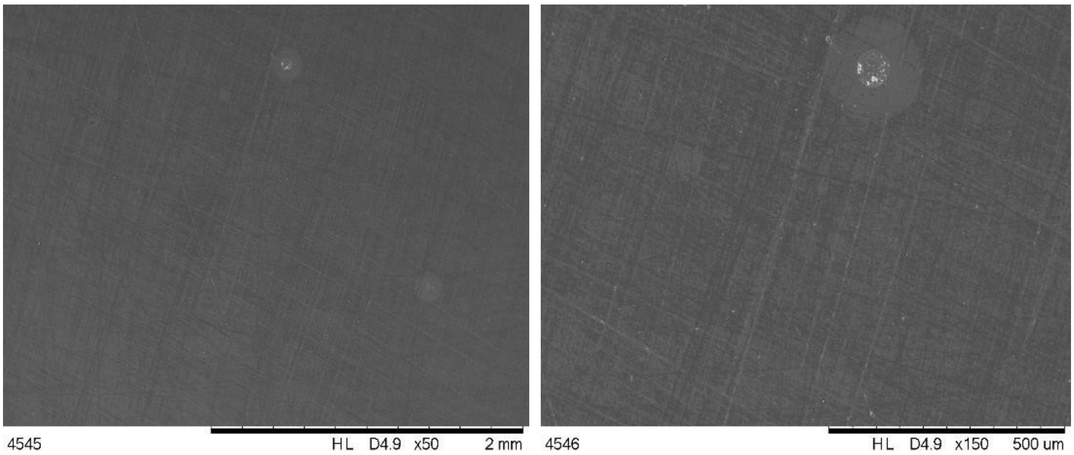

*Fig. 6: Samples containing 5 % of organic phase (1st extraction) OP1*

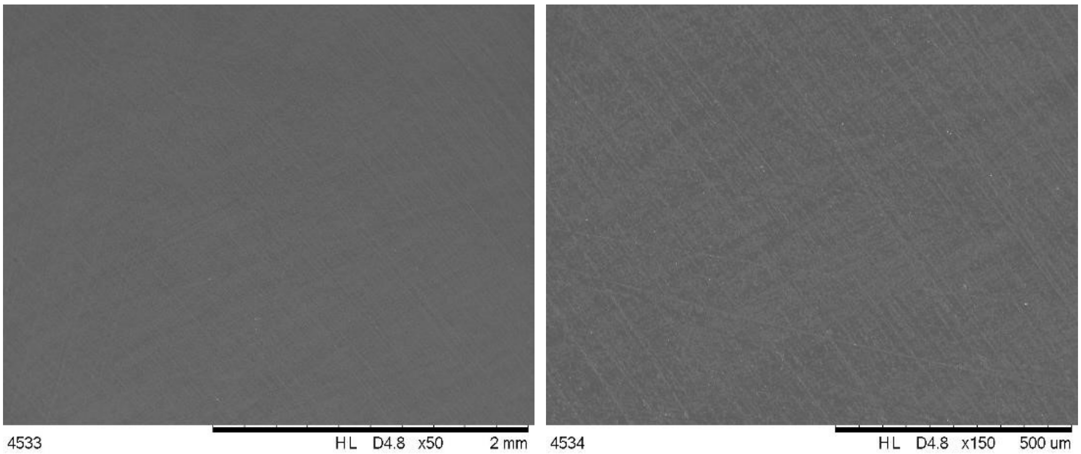

*Fig. 7: Samples containing 10 % of organic phase (1st extraction) OP1*

For the organic phase following the first extraction, all samples at 5 wt.% (Fig. 6) and 10 wt.% (Fig. 7) displayed a homogeneous structure without any precipitation. The observations of the samples microstructure cross section did not exhibit any visible porosity.

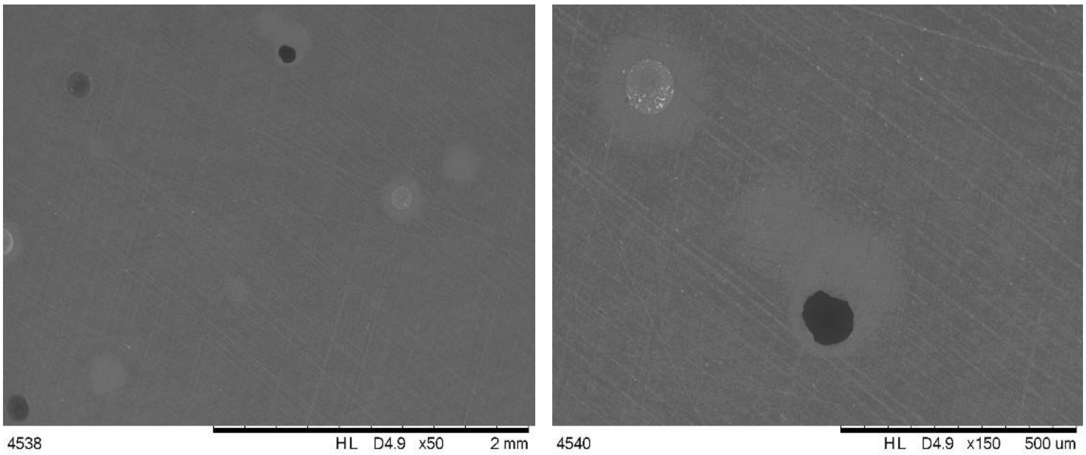

*Fig. 8: Samples containing 5 % of organic phase (2nd extraction) OP2*

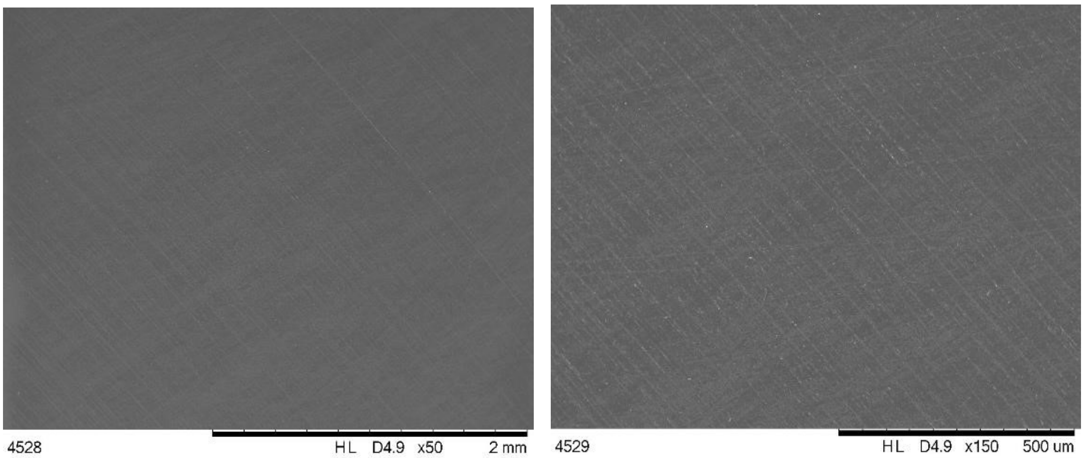

*Fig. 9: Samples containing 10 % of organic phase (2nd extraction) OP2*

In contrast, for the organic phase after the second extraction, samples at 5 wt.% (Fig. 8) revealed local pores within the microstructure, while the 10 wt.% sample (Fig. 9) showed a more uniform and homogeneous structure.

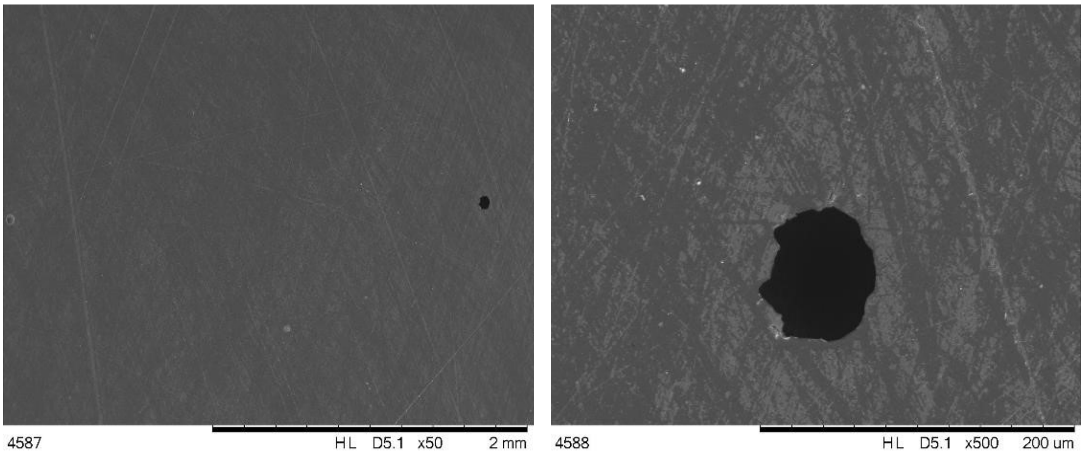

*Fig. 10: Samples containing 5 % of aqueous phase (2^nd extraction) AP2*

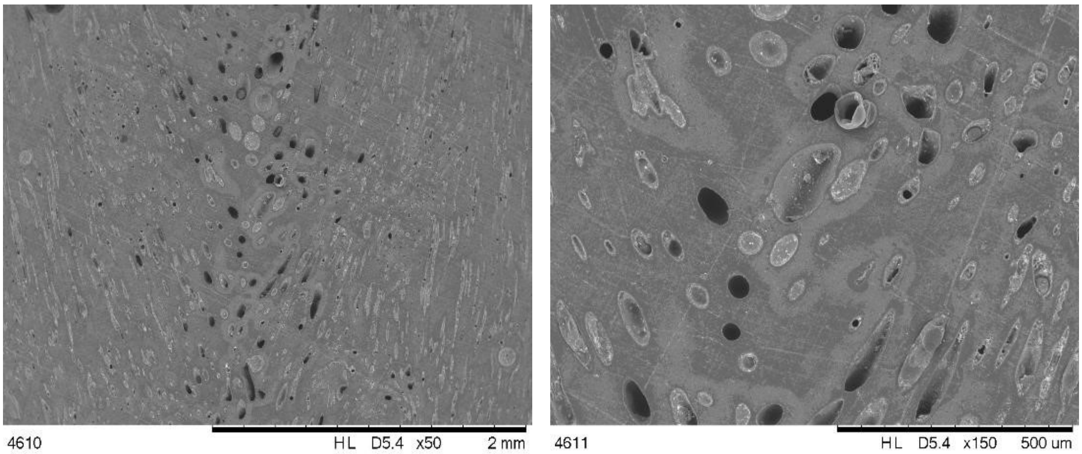

*Fig. 11: Samples containing 10 % of aqueous phase (2^nd extraction) AP2*

For the aqueous phase after the second extraction, the 5 wt.% samples (Fig. 10) exhibited a minimal number of pores, whereas the 10 wt.% sample (Fig. 11) contained numerous pores and precipitates. The precipitates had an oriented, elongated shape, with the largest pores concentrated in the centre of the sample.

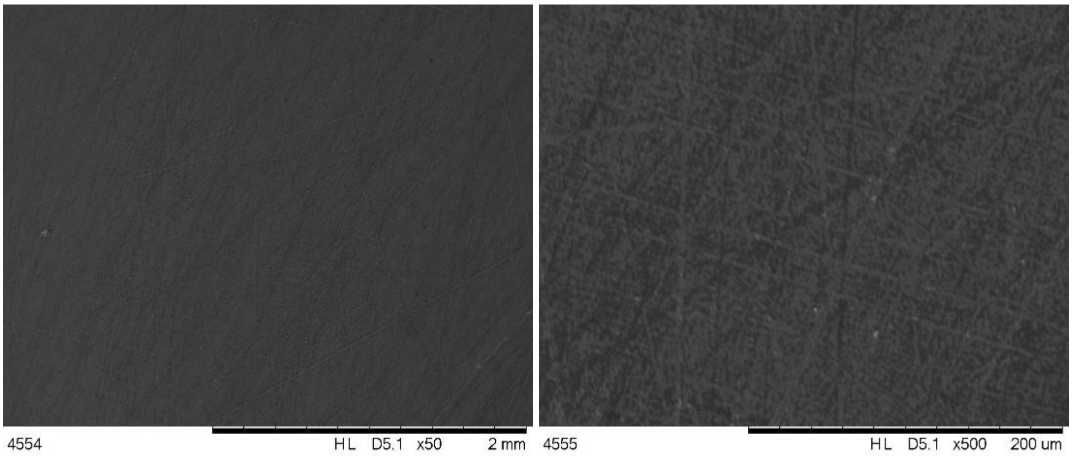

*Fig. 12: Samples containing 1 % of solid fraction recovered (SF)*

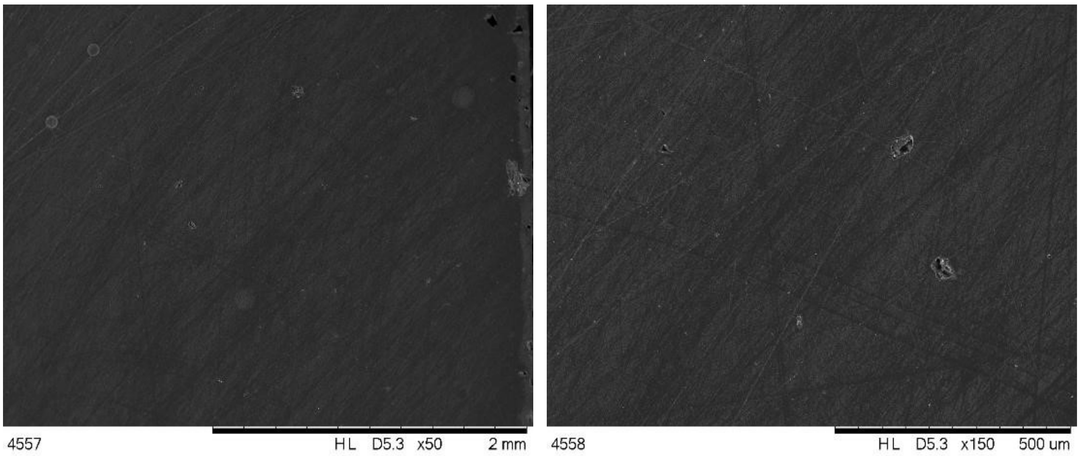

*Fig. 13: Samples containing 5 % of solid fraction recovered (SF)*

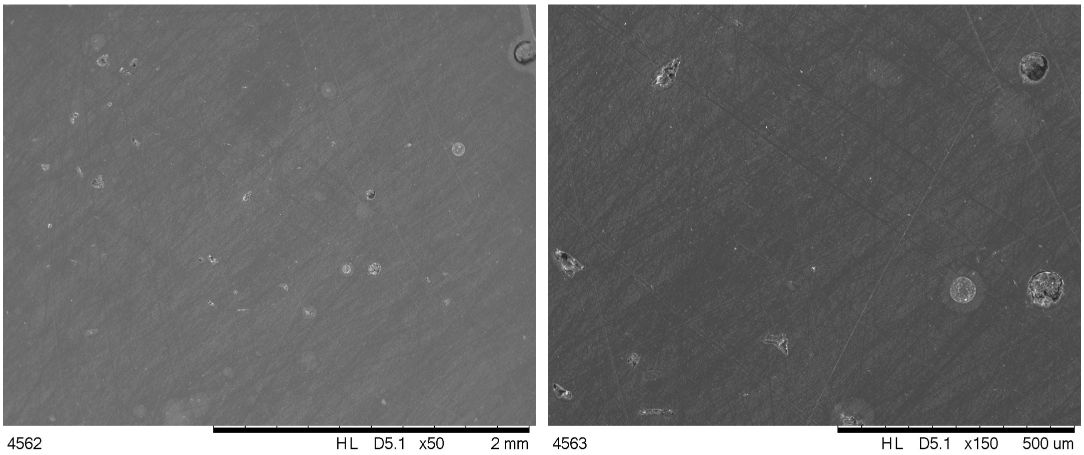

*Fig. 14: Samples containing 10 % of solid fraction recovered (SF)*

The cross-sections of the samples with solid fractions recovered through evaporation at concentrations of 1 wt.% (Fig. 12) and 5 wt.% (Fig. 13) exhibited a homogeneous structure without visible porosity. However, a 10 wt.% addition resulted in noticeable oval shaped precipitation in the size ranging between 50 µm and 100 µm within the investigated sample's structure (Fig. 14).

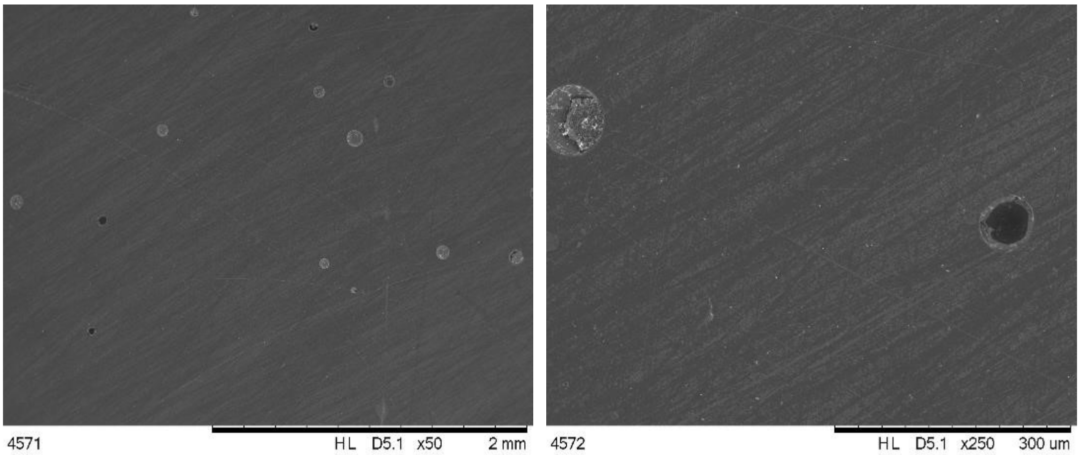

*Fig. 15: Samples containing 5 % of liquid fraction recovered (LF)*

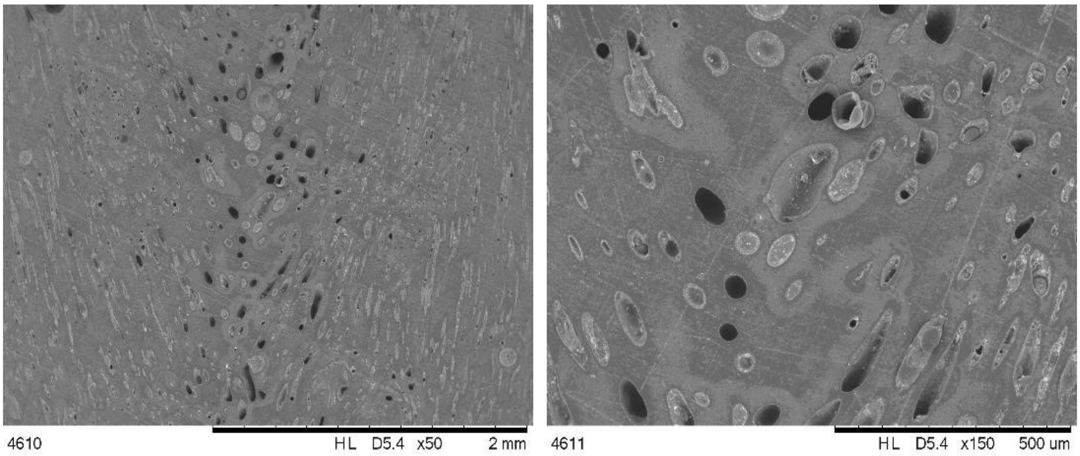

*Fig. 16: Samples containing 10 % of liquid fraction recovered (LF)*

Similarly to the aqueous phase, in the case of the liquid fraction following evaporation, samples with concentrations up to 5 wt.% (Fig. 15) showed a small number of pores. However, at a concentration of 10 wt.% (Fig. 16), a significant increase in pores was observed. The precipitates were oriented and elongated, with the largest pores located centrally within the sample. This clearly indicates a lack of compatibility between the liquid fraction and the amine-based epoxy resin, particularly at higher concentrations. This incompatibility was further reflected in the mechanical properties of the samples, where a reduction of approximately 50% in performance was observed when compared to the reference sample and samples containing 1 wt.% and 5 wt.% solid fractions.

# 4. CONCLUSIONS

The following conclusions can be derived after including the liquid recycled fraction derived from the solvolysis process in amine epoxy resin formulations and their characterisation:

Formulation:

- Seven different organic fractions were separated and investigated by means of mechanical tests, thermal (HDT) and microscopic observations (SEM). Separated fractions from the solvolysis process at different stages were neutralized fraction (NF), organic phase (1st extraction) (OP1), organic phase (2nd extraction) (OP2), aqueous phase (2nd extraction) (AP2), solid fraction recovered (SF) and liquid fraction recovered (LF) and aerial waste (AW). All fractions were delivered by project partner GAIKER, while chemical composition was characterized by CEA.
- Two different hardeners of NOMA resin systems namely MR and LRA were tested. Based on the results conducted with non-neutralized waste and not satisfying mixtures with the non-neutralized fraction, it was decided to focus on the system with LRA hardener.

Characterisation:

- Based on the conducted investigations, it was found that the best results i.e., addition of the organic fractions in the certain concentrations exhibited no negative influence on the mechanical and thermal (HDT) properties.
- It was found that the best concentrations of liquid fractions from all mixtures were exhibited by the samples contained neutralized fraction (NF) in concentration of 5 wt.%, solid fraction recovered (SF) in concentration of 1 wt.%, as well as liquid fraction recovered (LF) with 5 wt.%.
- The microstructures of above-mentioned samples were characterized by the small amount of the voids in the prepared cross sections which proved their optimal performance. These material compositions will be used for the fabrication of the demonstrators i.e., joining collets.