Theme 7 – TRANSPORT (including AERONAUTICS)

EURECOMP

Recycling Thermoset Composites of the SST

Grant agreement no.: 218609
Funding Scheme: FP7-CP-FP
Duration: 01 May 2009 – 31 July 2012

FINAL SUMMARY REPORT

The EURECOMP consortium

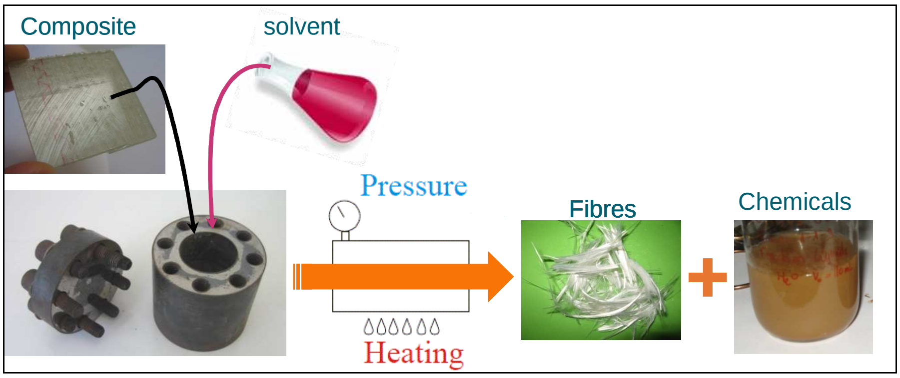
Beneficiary Number	**Beneficiary name**	**Beneficiary short name**	**Country**
1 (coordinator)	PLASTIC OMNIUM AUTO EXTERIEUR SERVICES	POAES	France
2	Volvo Technology Corporation	VOLVO	Sweden
3	XIETONG AUTOMOBILE ACCESSORIES	XTG	China
4	SACMO	SACMO	France
5	European Composites Recycling services Company	ECRC	Belgium
6	British Plastic Federation	BPF	UK
7	Uriarte Safybox S.A.	UREL	Spain
8	ICAM	ICAM	France
9	GAIKER	GAIK	Spain
10	University of Limerick	UL	Ireland
11	University of Exeter	UEXE	UK
12	University of Bristol	UBRIS	UK
13	COMPOSITEC	COMP	France

1) Executive summary

The goal of the EURECOMP project is to set up a new route to recycle fibre-reinforced thermoset composites.

In the surface transport industry, no really satisfactory way has been found so far for composite production waste and end-of-life products, in particular for thermoset composites due to their cross-linked three-dimensional chemical nature. The European legislation now requires to recycle this waste instead of landfilling it. The existing treatment solutions show limitations: incineration offers poor energy efficiency and generates polluting emissions, mechanical recycling only allows to recover lower performance reinforcements. As for feedstock recycling, that involves breaking down the polymers into low molecular weight species using heat (gasification and pyrolysis) and chemicals (solvolysis), it has only been applied to thermoplastics so far.

The EURECOMP project aims at developing the physico-chemical separation and recovery process called solvolysis, in order to recover the mineral fibres as a reusable reinforcement in new composite parts, as well as to convert the organic phase into small molecules that could be reused by the chemical industry. The objective is to define the best conditions for recovering products of highest possible commercial value.



The solvolysis process

In the first phase of the project, the main composite waste resources in Europe have been identified. Production waste, end-of-life boats and end-of-life vehicles represent the most reliable sources, even though the collecting and dismantling network of composites in end-of-life products still needs to be set up.

In parallel a laboratory prototype solvolysis reactor has been designed and built. The process parameters identified as influent are: temperature, processing time, pressure and composite mass/water volume ratio. Numerous solvolysis trials have been carried out in order to determine the parameters window leading to the best recovered products.

The first results showed that solvolysis allows to remove up to 90% of the resin, to retrieve a liquid containing potentially interesting chemicals, and to recover glass fibres with a satisfactory aspect. The products obtained, in solid and liquid phases, were then analyzed more thoroughly to assess the reuse opportunities by comparing their properties to the ones of original raw materials.

Analyses carried out on the liquid fraction show that the solution contains chemicals of potential commercial value, among which benzoic acid and some glycols. The analyses of the mechanical performances of the recovered glass fibres show that the mechanical properties are best preserved when operating at low temperature and shorter reaction times. It also appears that the fibres may need either resizing before reuse, or the choice of very specific reaction parameters allowing to retain a given resin coating on the surface.

During the second phase of the project, a large scale prototype reactor was designed and built. New solvolysis trials could be started, based on the optimized set of parameters identified during the trials on the laboratory scale reactor. Due to the new size of the reactor and to the different phenomena involved at this scale, some of the parameters had to be adjusted to obtain recycled fibres with sufficient mechanical properties.

A Life Cycle Assessment was conducted thanks to the data gathered on the large scale reactor. It reveals that the solvolysis process is not yet competitive with treatments like mechanical recycling or energy recovery, but can possibly be competitive with pyrolysis in terms of environmental impacts.

Finally, based on the recycled glass fibres obtained by solvolysis in the large scale reactor, new BMC compounds could be processed, incorporating an optimum percentage of recycled fibres beside virgin fibres. This allowed the industrial partners to mould real-size prototype parts and compare them with production parts.

The project has allowed to gain a better knowledge on the solvolysis technology applied to thermoset composites. The process still needs improvements before a new industrial scaling up in order to be economically more competitive.

2) Project context and main objectives

In the context of the European regulation on environment protection and waste recycling becoming always stricter, the EURECOMP project aims at proposing a new recycling route for thermoset composites in the sustainable surface transport. The European regulations encourage wherever possible the complete recycling of products and materials, and the avoidance of final waste to be landfilled.

Unlike thermoplastic composites, thermosets cannot be recycled throughout remelting due to their cross-linked three-dimensional chemical structure. The most common ‘recycling’ alternatives to date for thermosets are based on grinding the moulded components and incorporating the fine fractions into new composites as fillers. This mechanical methodology has been, by far, the most studied all over the world for this type of materials. Another treatment based on pyrolysis allows to recover mineral fibres and fillers, but does not allow to retrieve organic chemical components that could be reused for producing polymer resins.

Apart from mechanical recycling and pyrolysis, combustion for energy recovery and recovery in cement kilns (after combustion mineral fibres are reused in cements) are the only other available recycling paths. Energy recovery technologies transform the calorific value of waste into a type of energy. As many efforts have been made to limit the associated polluting emissions, this technology is growing considerably. However, this method could be considered as a ‘treatment for destruction’ rather than a recycling method, as it does not allow to recover useful raw materials for reuse in new products.

The solvolysis recycling process studied in the framework of EURECOMP consists in subjecting composite waste materials to hot water and high pressures in a reactor in order to separate the reinforcement fibres from the resin matrix, and to recover a liquid phase partly dissolved in water and partly non soluble.

The main objectives of the project are to demonstrate the scientific and economic feasibility of the solvolysis technology, to identify the processing parameters that give the best possible quality fibres, as well as the most valuable chemical compounds in the retrieved organic phase, and finally to test the recycled fibres in industrial parts.

The project also aims at identifying the most promising streams of thermoset composite waste in Europe, especially from surface transport, by identifying the size, nature and location of waste sources on the territory and assessing the collecting and treatment potentials. Eventually, the objective is also to disseminate information throughout Europe on the potential of solvolysis for recycling thermoset composites.

3) Main scientific and technical results

3.1. Waste stream Organisation

In order to provide a global view of the feasibility of composites recycling through solvolysis, upstream and downstream fields and markets were investigated. Through collaboration of partners inside the consortium and contacts outside, the composite waste resources was studied and allowed orientations of the project. The process was evaluated in terms of financial viability and environmental impact, the final markets and users were investigated and questioned.

3.1.1. Waste resource characterization

The first step of the EURECOMP project was to carry out an investigation concerning the waste resources to be recycled in order to give orientations to fundamental and experimental research about the nature of materials to be recycled.

Investigations were carried out for 12 West European countries about waste from transports, which includes production waste and end-of-life waste.

The nature of composites generated by the industry is known to be about 1/3 thermoplastics and 2/3 thermosets. Among the latest, polyester matrices represent approximately 75% of the volume and glass fibre remains the predominant reinforcement. This focused the project on the study of polyester/glass fibre based composites.

Considering production waste, the whole composite market was considered in order to aggregate volumes that can be used without distinction by the recycling process.

For waste created by production processes, 45kt was estimated to be generated in 2010 with growth to be considered similar to that of the global market. This resource is the most interesting one from the point of view of a recycling process, thanks to known composition, possible traceability and easy sorting possibilities.

When considering end-of-life waste, data about composite presence and treatment becomes rare. No or few dismantling operations consider composite as a material to be sorted and it is thus eliminated as a waste for landfill or incineration.

Vehicles impacted by composite recycling issues are end-of-life leisure boats due to high quantities present in their construction, mainly for the hull. Furthermore, end-of-life boats treatment represent an issue for harbours due to the environmental pressure, who begin to take actions in order to avoid boats to be abandoned or sunk. This sector is the most willing to be involved in a composite recycling scheme, the retrievable composite volume was estimated to be of a maximum 10kt/year in the near future if a solution is proposed.

Other transport products were initially targeted in the project but did not lead to interesting waste resources. Trucks and coaches undergo massive exportation after a 'standard' life. They are nearly never dismantled inside Europe, making their composite end-of-life parts out of reach. Automotive composite parts, despite an important market share in the composite market, represent a very low portion of a car composition; the volume is then completely lost among non valuable waste. For trains the situation is similar to that of cars, and composites are eliminated.

3.1.2. Recycling stream setting

In order to evaluate viability of the new recycling process, a global organisation was simulated from waste to reuse applications, based on experimental results, market investigations and industrial schemes.

A collecting system was established in order to supply recycling plants with the composite wastes from the identified sources. Geographical establishment of plants was defined considering the known waste distribution of France, which represents an average situation of European countries. Considering transportation and installation cost, it was found that two plants should be built in order to treat the volume from the area. The plants were equipped with all required equipment for waste preparation (cutting, shredding) prior to solvolysis process.

The plants were defined with several lines of solvolysis reactors in order to be able to handle the total volume of waste. This construction also offers the necessary modularity for installing more or less reactor lines in order to adjust the plant capacity.

After the reactors, a common line of fibre cleaning and liquids treatment was defined in order to retrieve the expected final products: recycled glass fibres and chemicals in solution.

3.1.3. Reuse of solvolysis products

The fibres were evaluated by the consortium in moulding compounds for electrical boxes and truck panel applications. The results showed the possibility to integrate them as replacement of 20% of standard glass fibres. Characterizations showed a technical level close the one of compounds with 100% virgin fibres.

Despite the fact that various separation techniques were tested to recover the chemicals obtained during the reaction, it has not been possible to separate efficiently the different molecules in order to reuse them. Several ideas have been put forward in order to reuse the liquids in the process and/or make energy recovery with these products.

3.1.4. Economic evaluation

Considering all the different operations necessary for recycling composites, from waste source to final product, the global cost of treatment and product was calculated. It appeared that the treatment cost would lead to a glass fibre cost higher than the price of virgin ones, which is not acceptable by final users. Process improvements were then designed in order to achieve more efficient production and should be tested in future experimentations.

The technology must first reach an economic equilibrium to be implemented at larger scale.

3.1.5. Environmental evaluation

The solvolysis technique was compared to other recycling techniques available for composites: cement kiln process, grinding process and pyrolysis process.

The final life cycle analysis (LCA) showed a lower environmental efficiency of the solvolysis process compared to mechanical recycling, but impacts quite close to the ones of pyrolysis recycling. Criteria like the contributions to climate change, human toxicity, terrestiral ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, or fossil depletion, have been considered and assessed for each technology.

Regarding the results of the LCA simulation, there are two hotspots associated to the solvolysis process: the energy consumption linked to the solvolysis reaction and the acetone required for the washing step. The use of an alternative solvent to acetone could also be studied in order to improve the environmental performance of the process.

This LCA allowed to identify the major weaknesses of solvolysis. Some optimisations in the global process could be proposed by the consortium and tested in the simulation. Even though solvolysis appears competitive with pyrolysis, it remains insufficient to reach the best impact level of the other technologies, like for instance mechanical recycling.

3.2. Solvolysis testing

The work package dealing with solvolysis testing aimed at developing the innovative recycling technology, setting up both the solvolysis process and the reactor best suiting the characteristics of the recyclable materials and the final applications for recovered products.

A first stage of this work consisted in a laboratory-scale approach, that would lead in a second stage to the subsequent transfer to a larger prototype-scale reactor in order to check for size effects.

The laboratory-level work was designed to allow changing the parameters of the solvolysis, such as pressure, temperature, time, reactants, *etc*, in order to obtain a good knowledge of the process. Using optimized experimental designs, we covered a wide range of variables: for example, pressure values can vary between 75 and 250 bar, and temperatures between 30ºC and 275ºC. These trials aimed at knowing the effect of these parameters on the process, and so, gave the opportunity to select different recoverable products after reaction, that should allow subsequent reliable technical and economic optimization of the technique. The results of these studies allowed to:

- Define the requirements for the prototype scale reactor
- Provide recycled glass fibres for testing reuse potential in composite compounds and composite parts,
- Analyse the organic solutions retrieved from the reactor.

Experiments also show that simple tap water can be used in subcritical conditions, which makes the process less complex and expensive than initially expected.

Through the various experiments we acquired knowledge on the solvolysis reaction using water-based solvents on polyester composites, which helped us identify the influence of the parameters of the solvolysis reaction on the nature of the obtained products.

3.2.1. Laboratory scale reactor

Different laboratory scale batch reactors were used, from 4 ml to 1l in capacity. It was shown that the obtained results were similar.

The 1l reactor was designed and built in order to process long strips of composites (up to 40cm), so that long fibres could be studied. The equipment features:

- A fast heating system, permitting to reach temperatures in the range of 300°C in only a few minutes
- A fast water cooling device in order to quench the reaction when the reactor is used in a batch mode,
- A pressure controlled exhaust system allowing pressure stabilized reactions and a controlled opening of the reactor under pressure.

The 1 liter solvolysis reactor and cooling device

3.2.2. Laboratory solvolysis of polyester composites

Using different small scale reactors, it has been shown that all the tested polyester resins are, as expected, hydrolysed to a sufficient extent in order to recover the fibres. Temperature and time must be adapted to the kind of composite. For example, highly calcium carbonate filled resins are much longer to hydrolyse. A compromise must be found since decreasing the temperature leads to glass fibres of better quality, as described in the literature, but increases the time of the process to industrially unacceptable values.

It has been shown that, on a simple orthophtalic resin, the hydrolysis was complete and allowed to recover the phtalic acid. The glycols were not stable enough under the used conditions and they are significantly converted to other molecules. Increasing the temperature favored secondary or side reactions. On an isophtalic resin, the results are not fully comparable, but using the same conditions, the hydrolysis is performed correctly. On a DCPD (dicyclopentadiene) modified resin, many more molecules are obtained, coming from the DCPD degradation.

It was shown that, in the studied range, increasing the temperature by 10°C will decrease the cycle time by a factor of roughly two.

The conditions used allowed recovering glass fibres. They still need to be solvent washed (using acetone) to be reuseable.

Using the knowledge acquired with the laboratory scale reactors, a 20 liters reactor was built, allowing to test scale up effects on experimental conditions, processing conditions and obtained products.

3.2.3. Prototype scale reactor design and building

The previously obtained results led to the requirements of a 20 liter reactor, mandatory to test scale up effects and to produce enough fibres for testing on industrial parts.

The 20 liters solvolysis reactor

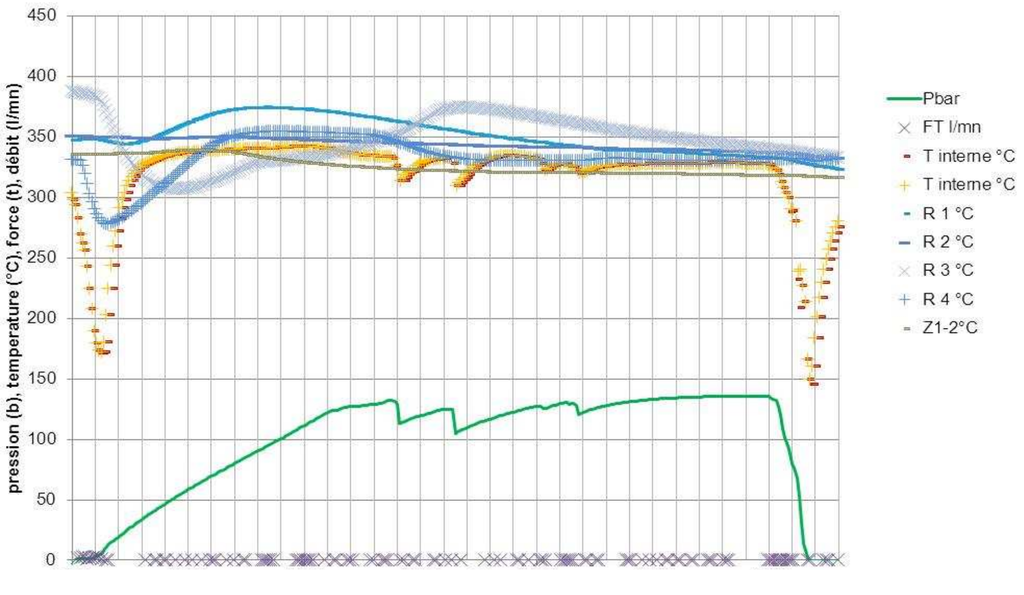
3.2.4. Prototype scale solvolysis of polyester composites

The experiments showed that, using the same temperature as the one used with the laboratory scale reactor:

- The heat diffusion/convection in the reacting chamber is longer than for the laboratory scale reactor;
- The size of the samples showed that the diffusion process is important and that bigger pieces of composites require longer processing times;
- The mechanical strength of the recovered fibres is strongly dependent on the maximum temperature reached during the solvolysis.

Indeed, due to the new size of the reactor and to the different phenomena involved at this new scale, some of the parameters had to be adjusted in order to obtain recycled fibres with sufficient mechanical properties.

Fibres were then produced for the other tasks of the project, allowing to test them on new composite compound samples for mechanical characterization, and to mould prototype industrial parts.



Pressure and temperatures recording during a typical cycle.

As seen below, the size of the composite pieces placed in the reactor has an influence on the cycle time. The picture below shows that the resin is removed along the sides of the sample and that it is still present in the inside, preventing the fibres from any separation. A few more minutes will end with a full separation of the fibres from the resin and a solvation of the organic molecules.

Evidence of diffusion, the resin is removed from the sides of the samples, not from the inside (50 x 50 mm).

Increasing the maximum temperature, even during a short time, is damaging the fibres. A stable temperature of 270°C leads to a 30% drop in mechanical strength, the Young modulus remaining unaffected. So, a compromise or an optimization must be found between cycle time and mechanical properties of the recovered glass fibres. It was also observed that, like with the laboratory scale reactor, increasing the temperature leads to smaller molecules, favoring secondary reactions.

Globally, the solvolysis trials carried out both at laboratory scale and on the large scale prototype reactor have helped identify optimized processing parameters (time, pressure, temperature…), leading to the recovery of fibres of quite good mechanical properties and to some predictable chemical reactions and products. The process is now better controlled both at laboratory scale and in the 20l reactor.

3.3. Reaction products analysis

The recovered products obtained in the solvolysis reaction were analysed to assess the real possibilities offered by their properties compared to original raw materials, *eg* quality, quantity, and identify suitable reuse opportunities.

This overall validation was performed in three different main activities:

- The first one provided a thorough analysis of the liquid fraction
- In the second, the solid compounds were analyzed
- In the third task, feasibility of recycled fibres for industrial parts manufacturing was evaluated and industrial applications were identified.

3.3.1. Liquid solution recycling

The composition of the liquid fraction obtained depends on the solvolysis reaction conditions. Analyses carried out at the University of Limerick (Ireland) show that the liquid fraction contains chemicals of potential commercial value, among which benzoic acid and some glycols. Benzoic acid was selected as the preferred solvolysis product due to its potential reuse applications, to the fact that the processing conditions can be controlled to obtain this product, and to its high commercial price, €450-900 /tonne depending on purity.

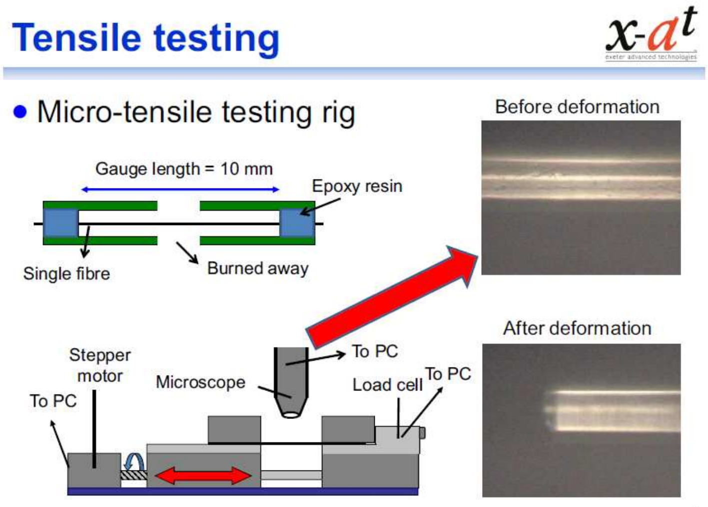
Nevertheless, the chemical analysis also revealed the presence of numerous different chemical components, each of them in low quantities making it difficult to separate efficiently valuable products. This is why the possibility of reusing directly the liquid solution obtained from solvolysis was also envisaged.

3.3.2. Fibre/filler analysis

The effect of the solvolysis conditions on the properties of the recovered glass fibres has been investigated.

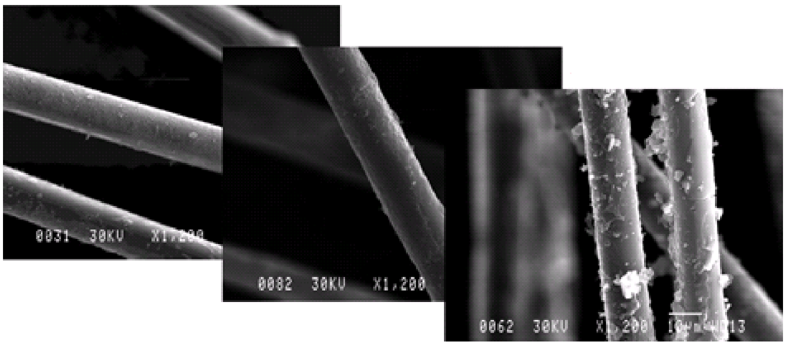
Analyses of the mechanical performances and of the surface quality of the recovered fibres were carried out at the Universities of Bristol (UK) and Exeter (UK). The chemical attack of water has a detrimental effect on the overall mechanical performance. These recovered fibres can retain up to a maximum of 60% of the mechanical performances of virgin fibres.

The main findings regarding the influence of the solvolysis conditions are that combinations of lower temperatures and longer reaction times result in better fibre mechanical performances. It also appears from the surface analysis that the fibres will need either re-sizing before reuse, or very specific reaction parameters allowing to retain a given residual resin layer on the surface.



Tensile strength measurement on recovered glass fibres

Microscopy analyses showed that resin fragments were identified on the surface of certain glass fibre batches, but that for some fibres the surface could be as clean as a virgin fibre surface if more water is used for the solvolysis reaction.

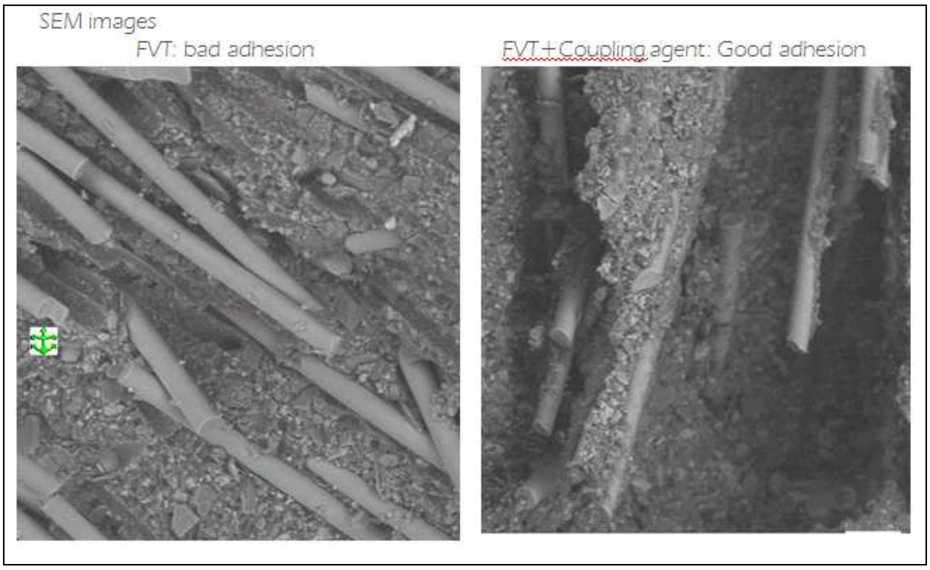


Surface analysis of solvolysis recycled glass fibres

3.3.3. Samples manufacturing and testing

The feasibility of using recycled chopped strand fibres for different parts manufacturing was studied and industrial applications were identified.

In order to improve the adhesion between recycled fibres and polyester matrix two ways were studied: the refunctionalisation of recycled fibres, and the incorporation of coupling agents in BMC materials. The results showed that the adhesion of recycled fibres can be enhanced by refunctionalisation and by using a coupling agent in the composite formulation.



SEM images showing adhesion between recycled fibres and matrix in the new BMC compound, without and with coupling agent

Recycled products were incorporated into a BMC material, a 20% of recycled fibres in total reinforcement showed similar mechanical properties than the commercial BMC compound used for manufacturing electrical box by Uriarte.

Other possible applications were detected and studied: replacing a chopped strand mat in a hand layup composite, using the fibres in raw materials to manufacture construction boards or core materials for sandwich composites.

Potential reuse applications identified for the solvolysis recycled glass fibres

3.4. Validation on large parts manufacturing

The recovered fibres were reprocessed in new composite materials for industrial parts. Prototypes of electric box and truck parts were manufactured with a content of 20% of recycled fibres. The real possibilities of upscaling these materials were assessed. Neither a change in process parameters nor an investment in extra equipment were required for the industrial manufacturing of these compounds. However the processes must be refined in order to improve the finishing when required.

The mechanical properties required for electrical box application were achieved. Regarding the truck front panel, the mechanical tests showed a degradation in performances. This needs to be compensated by other material and process improvements.

Prototypes of electrical boxes obtained with a EURECOMP BMC

4) Potential impacts, main dissemination activities

4.1. Potential impacts

The EURECOMP project opens new recycling perspectives for the thermoset composites, that represent the two thirds of the composite materials produced in Europe today. The initial objective to divide the cost of thermoset recycling by at least two has not yet been achieved, but the feasibility of the technology has been demonstrated, as well as the possibility to reuse the recovered glass fibres in new compounds for moulding new parts with satisfactory properties in some industrial sectors.

Recycling is a strategic issue for the European composites industry. After a few years of fine tuning, the solvolysis process could lead to the installation of a great number of solvolysis processing plants throughout Europe, thus generating employment and possibly avoiding relocations outside Europe. The life cycle assessment has also showed that the environmental impact of the solvolysis can be competitive compared to existing recycling technologies such as pyrolysis. Nevertheless, due to the low price and the high properties of the virgin glass fibres, the process would likely be more economically viable for the recycling of carbone fibres which have a higher economic value. A new collaborative project is being set up in order to assess the recycling of carbon fibres using solvolysis. Some more work must be done to consider the complete technical environment of the reactor and the reprocessing of the fibres. The large scale prototype reactor will be the basis of this new project.

Apart from waste management, the near future will be characterized by steep rises in the prices of raw materials, partly due to increases in oil prices. As the solvolysis technology can help, with further fine tuning, to provide ‘new’ organic and inorganic raw materials and to reduce landfill disposal, the European composites industry could find more opportunities to slow down the increase in the prices of their products. This can in turn help retain competitiveness in Europe, compared to low labour cost countries.

From a wider societal point of view, the recycling route offered by the solvolysis technology will allow to reduce the overall environmental impact of composite waste and to improve the quality-of-life of European citizens.

4.2. Main dissemination activities

In order to inform the players of the composites industry about the existence and advancement of the EURECOMP project, various articles and newsletters have been published by the partners: an article about the launch of the project in Reinforced Plastics magazine, articles in newsletters on partners' websites, an article in JEC Magazine. Information on the project has reached over 5000 people throughout Europe, in particular via the EuCIA website (www.eucia.org) from which the invitations to the training and demonstration sessions were sent.

Dissemination was also performed through partners' presence at numerous events. The project was displayed in more than 30 professional fairs and workshops oriented towards industrial companies, such as JEC, Plastpol, Plastics Recycling, etc. Talks were given at international conferences and workshops, three scientific papers were written in scientific journals.

Conferences where the EURECOMP project was presented:

- 3rd European Maritime Day, Gijon (Spain), May 21, 2010
- AMPT (International Conference on Advances in Materials and Processing Technologies), Paris, October 25, 2010: Scientific presentation and article about solvolysis testing and results
- Colloque Matériaux, Nantes (France), October 18, 2010
- Netcomposites workshop "End-of-life Options for FRP Composites", Chesterfield (UK), October 9, 2010: Presentation of technical achievement about fibres
- 18th International Conference on Composite Materials, Korea, August 2011: Scientific presentation and article about fibres mechanical testing and results
- European Conference on Composite Materials (ECCM 15), Venice (Italy), June 24-25 2012: Scientific presentation and article about fibres recoating.
- EuPC Recycling seminar, Brussels, January 9, 2012
- Irish Adhesion, Surface Science and Composites workshop, Limerick (Ireland), May 24, 2012.

At the end of the project, more specific and targeted information was transmitted to the attendees and participants to the EURECOMP training sessions held in Bilbao (Spain) on the 23rd of February 2012, in Brussels on the 22nd of May 2012, and in Nantes (France) on the 5th of June 2012, the latter being a demonstration of the prototype reactor. Interested companies proves to be from various industrial sectors, including boatbuilding, small trucks, aeronautics, production of composite pipes…

Finally a PhD thesis was completed and the results allowed a better understanding of the observations made on the chemical reactions involved in solvolysis.