Technology Overview

New Developments in Self-Reinforced Polymers

Content

Project Overview

Esprit was an SME targeted collaborative project part-funded by the European Commission. It had 12 partners from 8 European countries and a total budget of nearly 6 million euros. The project had a duration of 3.5 years, the end date being March 2012. Composites are now a well-established and continually evolving set of materials stretching from high-spec aerospace to biodegradable bio-based composites. This project used as its theme the development of Self Reinforced Polymer composites (SRPs) which are an all-thermoplastic composite based on the principle of having a reinforcement and matrix of the same basic polymer family which offers the advantages of being lighter in weight for equivalent stiffness, having improved recyclability and much improved impact resistance. There exist many applications where SRPs can potentially replace standard unreinforced polymers or glass-reinforced thermoplastic composites.

However, the current state of the art for SRPs is restricted to flat sheets or fabrics which limits the applications it can be used for. This project therefore, focussed on developing flowing versions of SRPs and the complimentary processing methods. The aim was to make intermediate materials which could be processed by injection or compression moulding and to develop novel selective heating methods to facilitate more accurate heating of the matrix and not the reinforcement.

Meeting in Valencia

With this in mind the overall aims of the project were

- Reduce plastic needed for a component by 30% (and hence the weight)
- Gain 3 to 5 times stiffness improvement over unreinforced polymers
- Create flowing SRPs in polyamides, polyesters and polyolefins
- Develop the ability to use SRPs for injection and compression moulding
- Develop selective heating of the matrix
- Produce complex moulded case study parts

Several avenues of development were pursued in the attainment of these goals and the most significant results are shown in more detail in this document. Certainly the process of creating the intermediate materials was very successful with Comfil and Celstran (Ticona) producing pellets and Fibroline making sheets, with and without heating susceptor additives. Compounding of heating susceptors was advanced by AIMPLAS with excellent distribution of additives, critical for the success of electromagnetic heating and Polisilk provided fibres and tested many thermal stability methods on reinforcements. Induction heating was proven viable and controllable by IVW with Fricke and Mallah and NetComposites showing efficient and innovative microwave based heating systems. A complete new dual-channel dynamic heating system was developed by Regloplas which allows super-quick cycling of tools from hot to cold and with an added unique energy battery development to improve efficiency. The partners given the tasks of moulding development optimised moulding parameters, produced case studies and tooling. PEMU produced parts and extruded SRP sheet, whilst Promolding analysed the injection process, produced demonstrators and manufactured tools. Finally AVK provided dissemination and access to the European Association of Thermoplastic Composites (EATC) who in turn provided industrial trials on commercial products. A true collaboration!

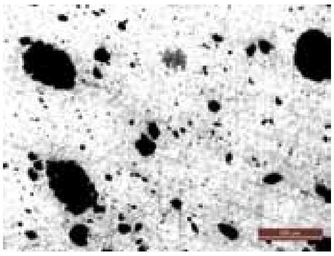
Compounding - The Art of Mixing and Improving Properties

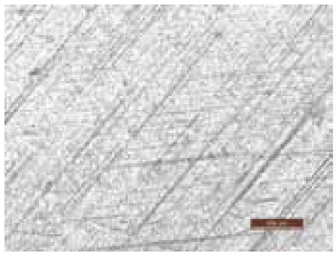
Compounding is a technology that involves the dispersion and distribution of fillers, additives, and substances into a polymeric matrix. The final result of this mixing process is a thermoplastic composite. The combination of microwave susceptors (nano-scale additives) with polymers can provide faster and more effective heating under microwave radiation. Several candidates like titanium dioxide, carbon black, silicon carbide, PZT, nickel, iron oxide, and carbon nanotubes were tested. Carbonous particles showed the best behaviour as heating promoters, especially carbon nanotubes, whose special nanometric structure provided an amazing heating efficiency.

A critical issue for the compounding process is the dependence between the additive dispersion quality with microwave heating efficiency, as well as the effect on down-stream processing requirements (melt spinning, extrusion and thermoforming).

Carbonous particles usually show significant problems during the compounding process, generating (relatively) huge agglomerated structures (up to 100 or more microns of diameter) that reduce the additive effectiveness and processability. A critical target of the work was to improve the dispersion quality by removing or minimizing the agglomerates size during the compounding process.

The most important parameters during the dispersion were the screw design and the mechanical energy. The efforts were focused on the study of their influence in the agglomerated structure and density. The research results were very successful, with excellent dispersion quality and the size of the agglomerates were eventually brought below 5 microns in diameter. These results facilitate an amazing heating effectiveness (beyond 80%, higher than other traditional heating processes that hardly border on 50%) even at low carbon nanoparticle contents.



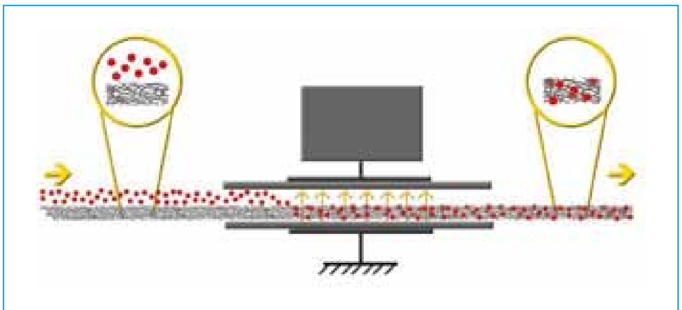


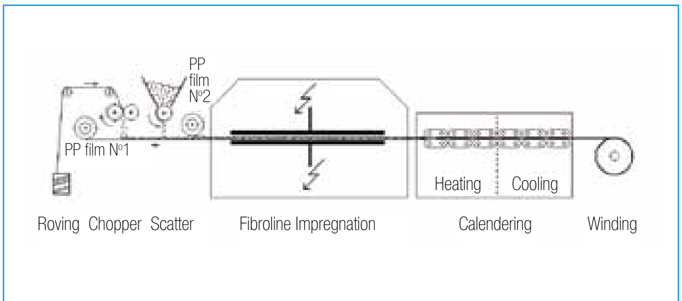
Very significant improvements in additive dispersion were achieved

It should be noted that working with nanoparticles also requires taking important safety measures. It is mandatory to use protective clothes, glasses and masks with suitable nanoparticles filters. However, once the particles are included in the polymer matrix the further processing requires no special protection. Processes such as finishing and the end-of-life disposal are the subject of separate research and the knowledge of these new materials is progressing all the time.

Powder Impregnation

Fibroline has pioneered a radical new manufacturing approach to composites and fibre reinforced materials in general. Its revolutionary dry powder impregnation technology greatly reduces the direct materials cost and the ecological footprint in composites manufacture, and enables the development of new products with specific functionalities and material characteristics.





The Dry Powder Impregnation Process

Fibroline uses a high voltage generator to electrically charge powder particles in an AC current field, and distributes them throughout any kind of porous structure (nonwoven, fabrics, foams etc). The types of powder include thermoplastics, thermosets as well as inorganic fillers and a broad range of additives and functional powders.

The main advantages of the Fibroline dry powder impregnation process are the possibility to manage the powder location and distribution. The environmentally sensitive technology requires neither water, not solvents, and reduces the cost of energy and the investment in pollution disposal processes overall.

In the case of the ESPRIT project, a global line has been adapted in order to produce self reinforced thermoplastic sheets based on:

- Long or continuous, randomly spread or aligned, high tenacity fibres thanks to a specific fibre placement process
- Thermoplastic powders with a chemical nature close to those of fibres used

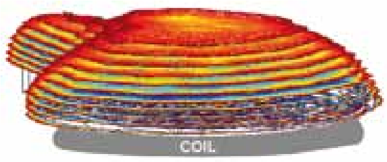
The reinforcement yarns can be continuous or cut according to the level of performance needed and the complexity of the end product shape (whether it is a necessity to have fibres flowing during the compression moulding of the final part).

As an example, based on polyolefin grades of fibres and matrixes, a flexural modulus can be achieved between 1.5 and 4.0 GPa according to the fibre configuration. Maximum flexural strength can reach 100 MPa for UD (unidirectional) structures and the maximum impact forces (ISO 6603-2) are close to 5000 N.

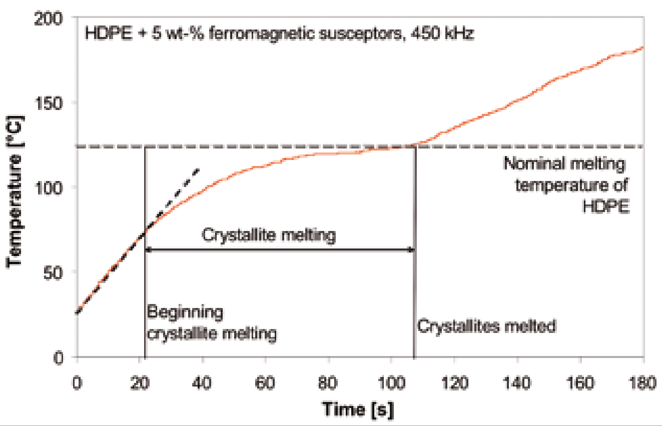
For polyester-based grades, flexural modulus and strengths varied respectively from 3 to 8 GPa and from 50 to 250 MPa according to the reinforcement type.

The main advantages of such products are the density, the impact resistance, the recyclability and the simplified, flexible process compared to existing technologies based on coextruded or hot-compacted woven fabrics.

Induction Heating



Magnetic field distribution of an induction coil



Exemplary temperature evolution of an inductively heated HDPE sample with ferromagnetic susceptors

Induction and microwave heating methods are based on the principles of energy transfer by electromagnetic radiation. The radiation activates susceptors which transfer the heat energy via conduction to the surrounding material. These techniques were chosen by IVW for the Esprit project to prevent a reinforcement melting by benefitting from the selectiveness of the susceptors. To that end, the susceptors are only distributed within the radiation-transparent matrix in order to limit the heating effect on the meltable polymer reinforcement.

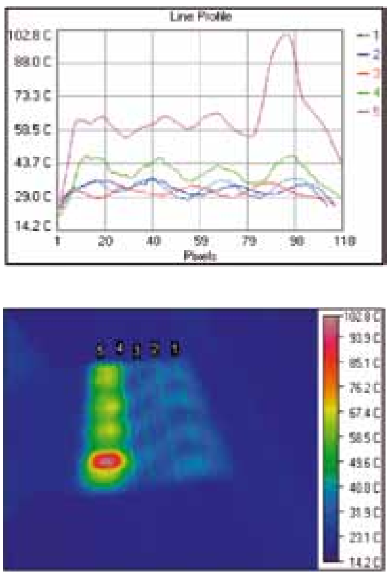
For induction heating, an alternating current causes an alternating electromagnetic field in a copper coil, which affects the susceptors in the material. The coil frequency lies between 200 and 700 kHz. In a first step, the main influences were investigated to optimise parameters. The results have revealed that the heating effect primarily depends on susceptor material, susceptor size, susceptor distribution and filler degree within the matrix, coupling distance between coil and sample, as well as coil shape and generator power.

Good results were achieved with ferromagnetic particles at a filler degree of only 5 to 10 wt-% in the matrix. Self-reinforced semi-finished sheets were successfully heated without significant reinforcement damage. The particle induction method was able to achieve heating rates of 60 K/min and more. Nevertheless, the economic investments, especially for the inductive heating of large components, are relatively high. On the other hand, the benefits of this method include the realisation of a contactless, homogeneous, intrinsic heating with an accurate temperature control.

Microwave Heating

As with induction heating, the aim of the microwave heating development was to selectively heat the matrix part of the composite by means of susceptor additives, leaving the reinforcement relatively untouched. This is to overcome the relatively small 'processing window' which exists in SRP materials; the difference between the melt point of the matrix and the reinforcement.

Graph and thermal image of microwave heated sheets



Two approaches have been tried by a partnership of Fricke und Mallah and NetComposites.

Multimode Microwave Heating

This method uses a random pattern of microwaves in an attempt to achieve a more homogenous heating effect. The waves are distributed by antennas into a chamber, not dissimilar to a domestic food processing microwave appliance. Although this method was proven to heat polymers with additives, it was also shown to be relatively inefficient and inconsistent in its heating performance.

Monomode Microwave Heating

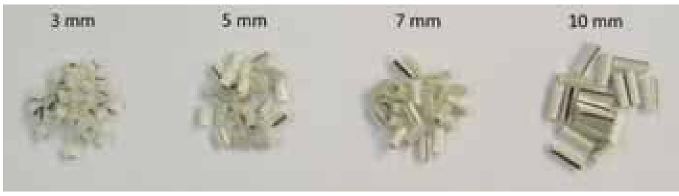
In this method a very controlled microwave is guided by tubes into fixed patterns. This has the advantage of being very efficient but it also produces very distinct hot and cold areas. In order to overcome this, two methods have been trialled in order to even out the heating effect. Firstly, a multi-antenna oven with a conveyor belt has been constructed in which the aim is to create an array of off-set heated stripes which combine to provide a homogenous heating effect. The second method is to manipulate the microwave to even out the energy distribution and therefore the heating. The former seems to be less efficient but trials are ongoing. The latter is very efficient but harder to control although, as the caption on the left shows, sheets have been successfully heated with good control.

The validity of using a selective microwave heating system has been shown and in the final stages of the project will be developed to a practical demonstrator standard.

Injection Moulding

Probably the most challenging aim in the Esprit project was to make flowing SRP materials which can be processed on conventional injection moulding machines. This has been achieved in controlled conditions and to attain optimal properties of Esprit materials some special attention should be paid to the injection moulding settings. Recommendations on preferred machine settings are given on page 10.

Esprit materials for injection moulding are produced by commingling and pultrusion (Comfil) or melt impregnation (Celstran) which results in cylindrical pellets in which the reinforcing fibres are as long as the pellet. In the Esprit project pellets of 3, 5, 7, 10, 15 and 20 mm have been produced and tested.



To study fibre distribution, orientation, final length, and the effect on the mechanical properties after injection moulding, pellets have been produced with a small fraction of black trace fibres. Using these trace fibres has shown that shorter fibres are easier to disperse evenly, which is important to achieve optimal properties. Typical pellet lengths are 5 and 10 mm, with a diameter of around 3 mm. The shorter 5 mm pellets are easier to process on smaller machines, for 10 mm pellets screw diameters of at least 40 mm or higher are preferred.

Due to the high fibre length and high fibre volume fraction the fibres will have difficulty to flow in extremely thin parts. Sections of a component that have a thickness of less than 1 mm may contain less fibres, leading to a locally lower stiffness.

Weld lines should be designed to be in non-critical areas, since the fibres cannot mix in the weld line zone, leading to potential local weakness.

Compression Moulding

Safety shoe cap manufactured by inductively heated HDPE/PP sheets

The developed semi-finished materials, especially fabrics and pellets, were processed by conventional compression moulding techniques. Pellets, with a wide melting temperature gap between matrix and reinforcement are able to resist an extruding step, which is a standard method for the processing of long glass fibre reinforced thermoplastics (LFT). By the adaption of this process, the ESPRIT partners have realized a processing method with polymer reinforcement allowing a complex shaped component to be manufactured. The viscosity of the self-reinforced materials is linked closely to the properties of the matrix, which results in similar composite viscosity as known from typical competing glass fibre reinforced materials.

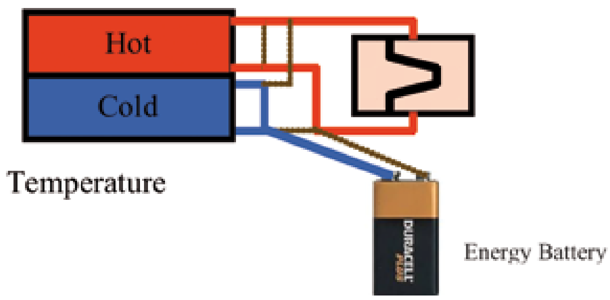
A standard compression moulding process for sheets was successfully realized by the use of the innovative RocTool® heating technology. This technology allows a fast heating and cooling based on inductive means. The cooling rates are especially crucial for the processing of highly viscous polymer-polymer materials – the hot tool increases the flowability, whereas the fast cooling under high pressure results in low shrinkage and good surface quality. Nevertheless, conventional tools can be used with self-reinforced polymers, but generally need longer cycle times.

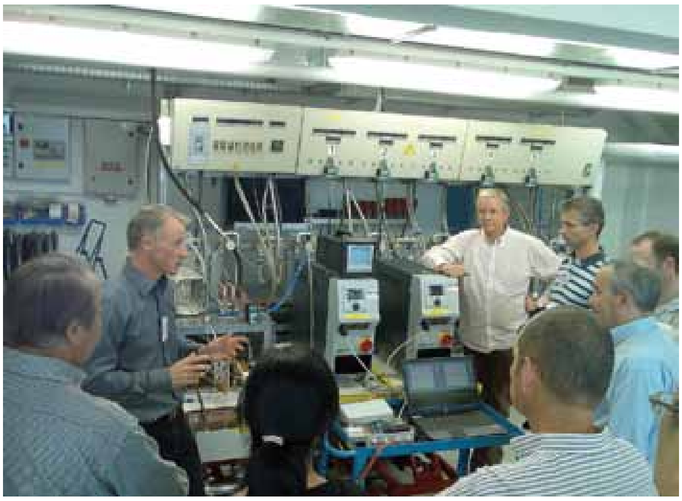
Automotive demonstrator part made of self-reinforced pellets

Dynamic Heating System

The Esprit project has been as much about processing technologies as it has about material developments. One of the unusual requirements for the moulding of some SRP variants is the need to heat and cool tools in a very controlled and rapid fashion. With conventional heating technologies such as oil or pressurised water there has been little requirement for the very accurate temperature cycling of tooling and therefore Regloplas have developed an advanced, integrated dual channel system.

Put simply, the system runs two channels continuously, one very hot and one very cold and switches between them by means of a complex and newly developed valve system. This system has to cope with rapid changes in temperature and pressure as, for example, super-heated water vapour is replaced by chilled water.





The new Regloplas system being demonstrated at an open day

This system uses standard Regloplas units linked by a new control and monitoring system run by a RT control unit or via a PC.

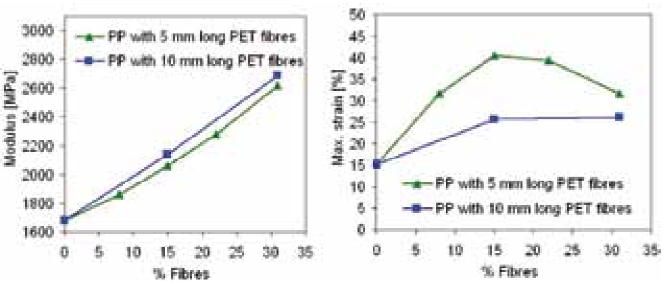
But there is a further innovation in the system as it contains a new concept called the 'Energy Battery'. This additional element acts as storage device for the chilled or hot water which is coming out of the tool meaning that rather than having to heat cold water or cool hot water the liquid is shunted into a 'battery' or storage device which holds it until required for the next cycle. This has the advantage of reducing the energy requirements and speeding up the tooling cycle time.

Such has been the pace of development that Regloplas can offer versions of this system by the end of the project, tailored to individuals needs. These can be suitable for water (max. 180°C) and oil (max 350°C) with the added advantage of improved surface finish and flow properties.

Material Properties

The Esprit SRP materials are characterized by a high stiffness to density ratio since they have similar density as the unfilled polymer, but a higher stiffness due to the addition of synthetic, polymer reinforcements of the same or similar family. The long fibres incorporated in the material use the effect that fibre pull-out upon impact dissipates a lot of energy. For example Esprit PP-HTPET (polypropylene matrix with high tenacity PET reinforcement) has a very interesting combination of high stiffness combined with extremely high impact strength at a low density.

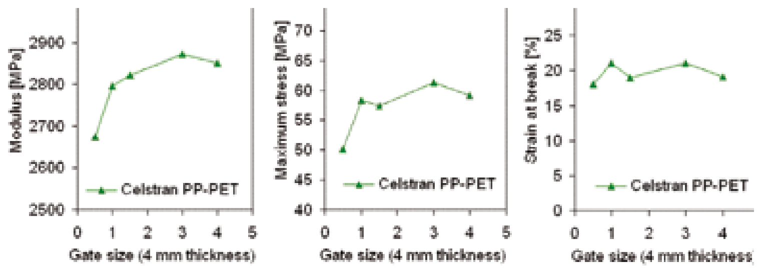
Typical properties attained with SRPP variants



Esprit materials give the best properties when the polymer fibres are not subjected to excess heat and shear. Therefore, the following settings for injection moulding have been developed which minimise the impact of the injection moulding process.

- Very slow feeding speed.
- Low back pressure, although some may be useful in dispersing the fibres.
- Flat temperature profile (nose may need a 10 °C higher temperature to prevent freezing). PP matrix: 170-180 °C. PBT matrix: 230 °C. LPET (low melt temperature PET) matrix: 180-190 °C.
- For materials with LPET matrix a well cooled intake zone (< 60 °C) is needed.
- Slow to medium injection speed.
- A large diameter nose, sprue and runners are advised. Esprit materials work well on cold and hot runners, as long as the diameter is large (a minimum of 3 mm).

Results of tests with various gate sizes



Fibres are visible in this post-test sample

Environmental Impact

The recyclability and sustainability of self-reinforced plastics has been compared to competing materials such as PP, GMT & SMC. The absence of conventional reinforcements such as glass fibre makes self-reinforced plastic relatively easy to recycle, making it particularly attractive in light of tough recycling legislation such as the European End-of-Life Vehicle Directive. Trials have demonstrated that self-reinforced plastic material waste can be introduced back into the manufacturing process at various levels and as the understanding of SRP processing progresses there are possibilities for completely closed-loop recycling options.

It is quite possible to take post-industrial waste, such as off-cuts and mouldings and remould them into different shapes with minimal loss of properties, and shredded self-reinforced plastic has be used as a reinforcing filler to increase the mechanical properties of unreinforced polypropylene. Post-consumer waste can be recycled using existing dismantling infrastructure and recycling technologies, being used for instance for injection moulding of commodity items.

The indirect benefits of these materials are the lower-weight products due to the reinforced nature of the SRPs but with no weight increase. Therefore glass reinforced PP could be replaced with PP reinforced PP (it may be slightly thicker but will be significantly lighter) or straight PP could be replaced with SRPP (the better stiffness-to-weight ratio means thinner, lighter products)

It has to be noted that there is an energy cost involved in manufacturing SRPs compared to unreinforced polymers but the lifetime energy savings will outweigh them.

A green house fan: This product required excellent impact resistance, light weight and a more resilient, secure snap-fixing. Successfully delivered with a PET/ PP combination

A football shin guard tool in production. The SRP materials give a lightweight, stiff, impact resistance compression moulded product.

Partners

Publications:

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2. Bayerl, T.; Schledjewski, R.; Mitschang, P.: Induktive Erwärmung von Kunststoffverbunden über partikelförmige Additive. IVW-Kolloquium 2010, Kaiserslautern, November 16-17, 2010.

3. Bayerl, T.; Schledjewski, R.; Mitschang, P.: Induction Heating of Thermoplastic Materials by Particulate Heating Promoters. Polymers & Polymer Composites (2010), in press.

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6. Bayerl, T.; Valchev, H.; Natter, E.; Mitschang, P.: Processing of Long-Polymer-Fiber Reinforced Thermoplastic Pellets by Compression Molding. 11th International Conference on Flow Processing in Composite Materials (FPCM-11), Auckland, New Zealand, July 9-12, 2012, submitted for publication.

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11. Morgan, L; Flow moulding SRP composites - practical developments. Composites UK Conference, Manchester Conference Centre. May 5-6, 2011.

Esprit Consortium:

AIMPLAS, AVK, EATC, Celstran GmbH, Comfil, Fibroline, Fricke und Mallah Microwave Technology, IVW, NetComposites (coordinator), PEMU, Polisilk, Promolding, Regloplas.

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