

Project no.

NMP2-CT-2005-515769

Project acronym

BIOCOMP

Project title

**New classes of Engineering Composites Materials from
Renewable Resources**

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Priority 3 - NMP

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Support to the new knowledge-based and sustainable processes and eco-innovation

Summary Report *Publishable*

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BIOCOMP – Publishable Summary Report

1 Background

The Integrated Project for SMEs Biocomp aimed at new high quality bio-based composite materials to substitute synthetic plastics and wood. These materials in development should deliver a breakthrough in properties and use of engineering biocomposites. They comprise both, thermoplastic and thermoset materials derived mainly from renewable, natural resources composed of biopolymers and reinforcing natural fibers. Through knowledge management advanced methods are applied of control, processing, design and manufacturing of prototypes and demonstration parts.

The potential shortage of fossil fuel reserves will force future economies to extract their raw materials from renewable resources. Biomass will contribute in various ways, whereas second generation biomass (un-used plants, residues of bio-technology or biorefinery and residues of food production) should be preferred. These ways will include:

- Energetic use of materials:
 - Direct firing of biomass or mechanically derived components like pressed bio-oils
 - Materials produced by biotechnology: biogas, biodiesel, bioalcohols, etc.
- Biorefinery: extracted chemicals and carbohydrates by a complete breakdown of the structure used as both an energy and material feedstock.
- Materials made from renewable biomass resources, from extracted and recovered constituents (fibers and/or biopolymers, see Figure 1)

Industry currently favours the use of biomass for an energetic use of the directly harvested materials or that derived by mechanical or chemical modification, because this is strongly supported by governments.

Materials from biomass (plastics)

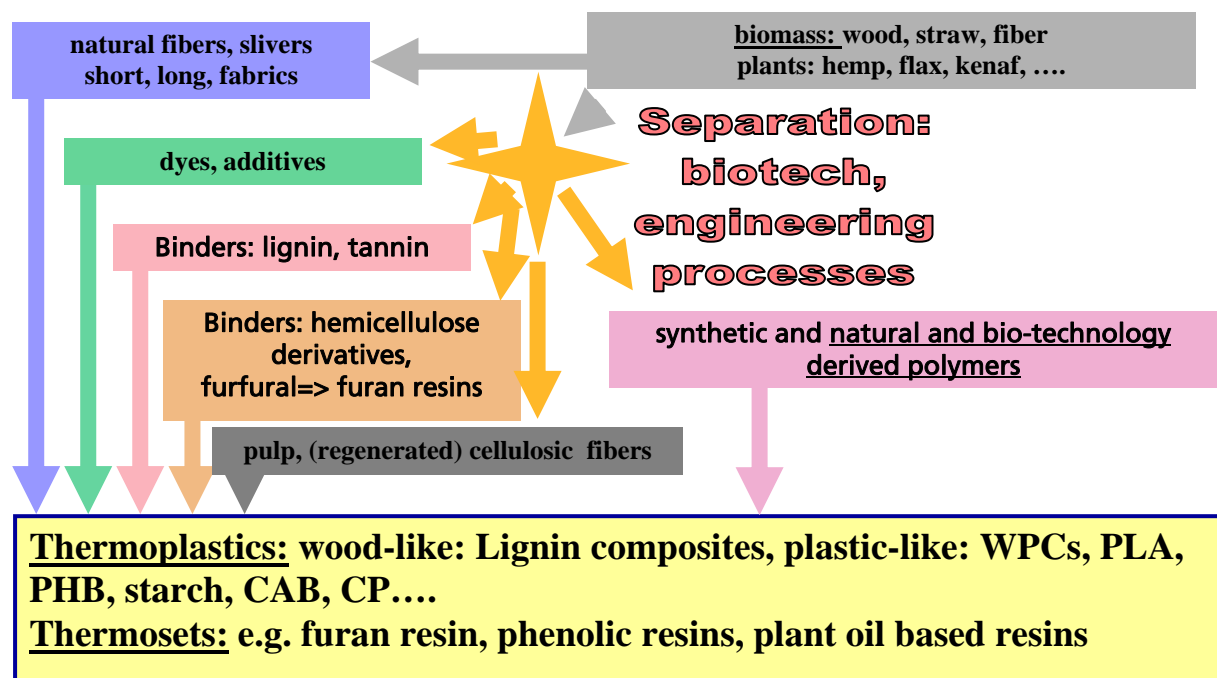


Figure 1: Scheme of biomass utilization for Biocomposites

Plastics industries manufacture a wide variety of materials, from which 99% of all plastics are produced or derived from major non-renewable energy sources such as crude oil, natural gas, naphtha and coal. These are used to meet both the requirements of cheap mass production and of highly specific applications. Biopolymers from various origins have already gained a substantial market share of the packaging market. Natural fibers cover soundproofing and heat isolation applications and are already used as an essential reinforcement for synthetic plastics such as wood plastic composites.

The combination of biopolymers and natural fibers would mean a further step ahead in utilization of bio-based materials, especially if engineering materials for challenging applications can be developed, which can compete with synthetic plastics. This step was in detail explored by Biocomp.

2 Objectives

Biocomp focused on biomass extracts to be directly used in engineering plastics or wood like materials applying only minimal modifications and including only additives from natural resources (Figure 2).



Figure 2: Natural fibers (slivers, non-woven and woven fabrics) for engineering part manufacturing

The Biocomp project developed **engineering materials** for **mass consumer and structural applications** and the **demonstration** of the performance for various industrial branches. Additionally, the used processing methods and facilities, as well as the design procedures were identical to those used for synthetic plastics and composites enabling opportunities for immediate industrial mass production after final developments.

3 Activities of the IP-SME

The approach of the Integrated Project Biocomp included the development of thermoplastics and thermosets based on available biopolymers or precursors with the potential to achieve the challenging objectives. The reinforcing natural fibers are those available in Europe. Advanced methods of control, simulation and processing supported the development. Prototypes and demonstrators showed the performance of the materials in end-use applications. Education and training initiatives addressed the public awareness and skill of engineers and staff to be later involved in manufacturing. The key partners of Biocomp were SMEs because much of the manufacturing base of biocomposites within Europe exists within SMEs. These SME's were supported by high tech SMEs and research centres.. The activities, processing and materials within the project comprised:

- Biopolymers:
 - Thermoplastics: **lignin, exclusively developed in Biocomp, starch, polylactide (PLA) and polyhydroxybutyrate (PHB)** (to a lesser extent) are commercially available bio-technology but less so for challenging applications.
 - Thermosets: Innovative **furan resins** to be developed from furfuryl alcohol with properties far beyond the state of the art application of foundry industries, **crops oil resins** to be obtained by chemical modification of oils from biomass.
- Natural fibres:
 - Relying on European agricultural production: **hemp, flax, wood and cellulose regenerated fibers (CRF)** used as loose fibers and slivers for thermoplastics and
 - Loose fibers, non-woven mats and fabrics for thermosets to give added structural properties.
- Fiber improvement:
 - Cutting, cleaning, pelletizing of available loose fibers according to processing needs
 - Selection of **fabric and non-woven mats**
 - **Pre-treatment** by plasma, acetylation, bleaching and impregnation to improve adhesion
- Natural or eco-friendly additives for:
 - **Flame retardants** to meet the highest criteria for electronic equipment
 - Plasticisers and **impact modifiers** to compete with standard synthetic plastics in the target applications (Natural Rubber included as a bio-based impact modifier)
- Design/simulation:
 - **Control** of quality of raw material, processes, and final products by on-/inline Near Infrared Spectroscopy in addition to, standard analysis and testing
 - **Material models** to describe theoretically the mechanical behavior of biocomposites,
 - **Simulation of structures** using finite element analysis, **moulding** using mould flow analysis and **curing** modeled by cure kinetics and data sets from the materials tests
- Demonstrators:
 - Cover **industrial mass consumer branches** of automotive, electronics, construction and furniture
 - Show benefits and drawbacks of materials including the eco-friendliness by a comparative **Life Cycle Analysis**
- **Education/training:** teaching modules were developed for education (students), practical workshops organized for training (engineers, staff and material designers).

The **processes** applied to compounding and part manufacturing used only standard equipment of plastics manufacturing as listed in Table 1. **These industrially relevant methods successfully** achieved materials and products for demonstration. These include challenging aspects of strength, size and shape, wall thickness, fire resistance, acoustic properties and so on. The demonstrators concerned various industrial sectors that could open new markets for Biocomp materials (see Figure 3).

Table 1: Overview on processing methods related to the polymer and the applications

	Thermosets based on		Thermoplastics based on			
	Furan resins	Crops - oil based resins	Lignin	PLA	PHB	Starch
Processing	Compression, vac. infusion, hand lay-up, prepregs, SMC, BMC, RTM	Compression molding	Pelletizing, injection molding	Compounds, injection molding, LFT-D, direct extrusion	Compounds, injection molding	Compounds, injection molding
Applications	Large parts, equipment covers	Fiber boards, MDF	Decorative: car interior, loudspeaker	Commodities, car interiors, plates, panels, chair	Commodities sports equipment,	Construct. elements, interior parts
	Boats, furniture	Plates for construction, furniture	Decorative parts for commodities	Construct. elements, profiles	Equipment covers	Interior commodities

SMC=Sheet Molding Compound, BMC=Bulk Molding Compound, RTM=Resin Transfer Moulding, LFT-D=Long Fiber Technology – Direct Processing, PLA=polylactide, PHB=polyhydroxybutyrate



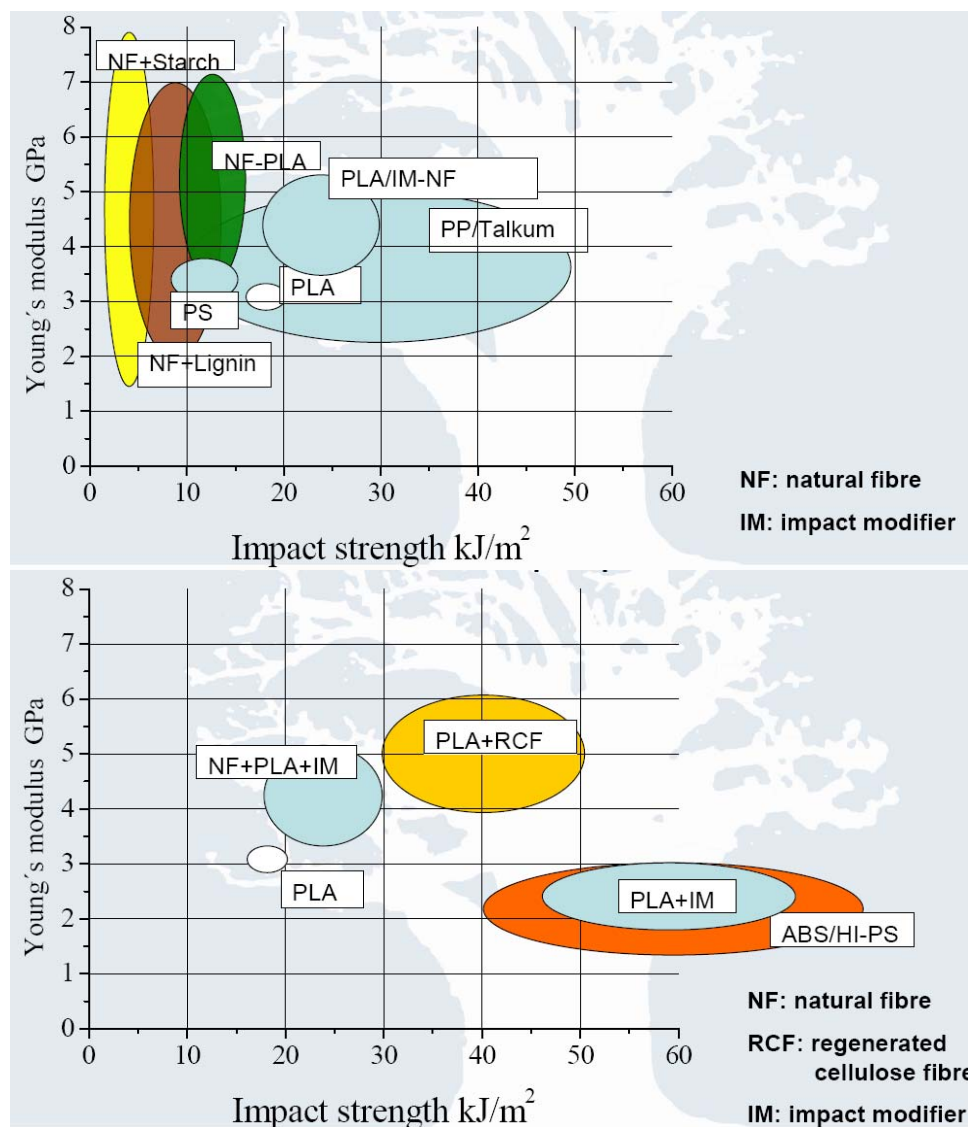
Figure 3: Model products of Biocomp materials: thermoplastics and thermosets

4 Materials overview

All materials experienced a strong technical progress within Biocomp with a target to achieve properties competitive to synthetic plastics. A Life Cycle Analysis could demonstrate substantial advantages above the synthetic counterparts.

Thermoplastics

The thermoplastic biopolymers lignin, starch, PLA and PHB were established as engineering composites for parts used in many commodities for various industrial branches. Their properties lie well in the range of PP/talcum, which is a widely utilized plastic in these fields (see Figure 4). Impact modified materials developed with innovative methods of long fiber direct processing (LFT-D) could surpass the challenging target of the project, an impact strength of 50 kJ/m^2 . Cellulose regenerated fibers increase impact strength without reduction of tensile properties of PLA composites. These materials can compete with ABS (AcrylonitrileButadieneStyrene) and HIPS (high impact polystyrene) often used for housings of equipment of electronics and automotive interior panels. Fire resistance could achieve highest classifications (UL94 V0, related to electronic equipment) for all types of thermoplastics with lower amounts of halogen-free flame retardants compared to synthetic ones.



PLA = polylactide, NF = natural fibers, IM = impact modifier, FR = flame retardant, RCF = cellulose regenerated fiber, (for reference synthetic polymers: PP = polypropylene, ABS = AcrylonitrileButadieneStyrene, HIPS = high impact polystyrene, GF = glass fiber)

Figure 4: Overview of mechanical properties of thermoplastic Biocomposites

Thermosets

The furan resins could be established as a new thermoset material for industrial applications to be processed by most standard methods of low cost and mass production of thermosets. Processing included: compression moulding, vacuum infusion, hand lay-up, BMC (Bulk Moulding Compound), SMC (Sheet Moulding Compound) and RTM (Resin Transfer Moulding). A comparison of various furan based materials is shown in Table 2. The values approach the range of glass fiber based polyester composites. The inherent temperature stability and fire resistance of the furan resins without additives is remarkable and opens the door to wide fields of applications. Excellent properties were achieved using carbon fiber fabrics for reinforcement where the application requires high stiffness.

Table 2: Mechanical data of materials by furan resins comparing formulations and processes

Composite material	Production method	Tensile properties	Flexural properties	Charpy impact	Fibre content
NF-Furan	Hot compression moulding failed	Str: 40 MPa	Str: 50-90 MPa Mod: 6 GPa	>10 kJ/m ²	70wt%
Glass-Furan	BMC	/	Str: 50-70 MPa Mod: 10 GPa	5 kJ/m ²	15wt%
NF-Furan	BMC	/	Str: 45-55 MPa Mod: 10 GPa	1 kJ/m ²	10wt%
Glass-Furan	SMC	/	Str: 100-140 MPa Mod: 9 GPa	50 kJ/m ²	50wt%
NF-Furan	Vacuum moulded prepreg	Str: 80-120 MPa Mod: 10-15 GPa	Str: 120 MPa Mod: 9-10 GPa	10-20 kJ/m ²	50vol%
Glass-Furan	Vacuum infusion/ Hand lay up RTM	Str: 160 MPa Mod: 10-15 GPa	Str: 200 MPa Mod: 9 GPa	45 kJ/m ²	40wt%

BMC=Bulk Moulding Compound, SMC= Sheet Moulding Compound, RTM=Resin Transfer Moulding, NF=natural fibers, Str.=strength, Mod = (Young's) modulus,

Maleinised natural oils emerge by the addition of maleic anhydride to the unsaturated fatty acid moiety of crops oils. The resulting biopolymer resins met the criteria of binders for **MDF (medium dense fiberboards) and HDF (High dense fiberboards) boards** with a wood fiber content of 70-80% (Table 3). While the mechanical properties of these biocomposite equivalents to MDF were somewhat lower than the specified ones, the significant advantage of the innovation is that they are completely **free of formaldehyde**. Concerning the planned use in furniture applications, future regulations will strongly support this aspect.

Table 3: Test results of the composite MDF-V3

	Characteristics measured	Unit	Values measured			Values required		
			min.	av.	max.	SR EN 622-5 MDF	SR EN 300 OSB	SR EN 312 PAL
1.	Density	kg/m ³	1097	1079	1111	> 600	> 600	> 600
2.	Moisture content	%	3	4	4	4-11	2-12	5-13
3.	Swelling in thickness after 24 h	%	4	6	11	max. 17	max. 25	max. 16
4.	Internal bond	N/mm ²	1,02	1,05	1,08	min. 0.65	min. 0.30	min. 0.45
5.	Bending strength	N/mm ²	18	24	28	min. 23	min. 20	min. 14

5 Knowledge based processing of materials to demonstrators

Demonstrators or model products are semi-finished or finished devices of a prototype character (about 20 are available from the project) that show the benefits of the developed materials but also their drawbacks, be it in manufacturing costs, time, surface finish, structural performance, acoustics etc.

5.1 Thermoplastics

Thermoplastics are processed using the methods outlined in Figure 5. Normally, compounding occurs on an extruder where the components are introduced by a feeder. The extruder heats these up above the melting point and homogenizes the melt by screws. A generated strand is then cut to form granules. Typically, twin screw extruders are used. Lignin processing runs via direct pelletizing (Figure 5) without heating to produce granules and thus saving significantly energy. An injection moulding machine forms parts in a mould from the granules.

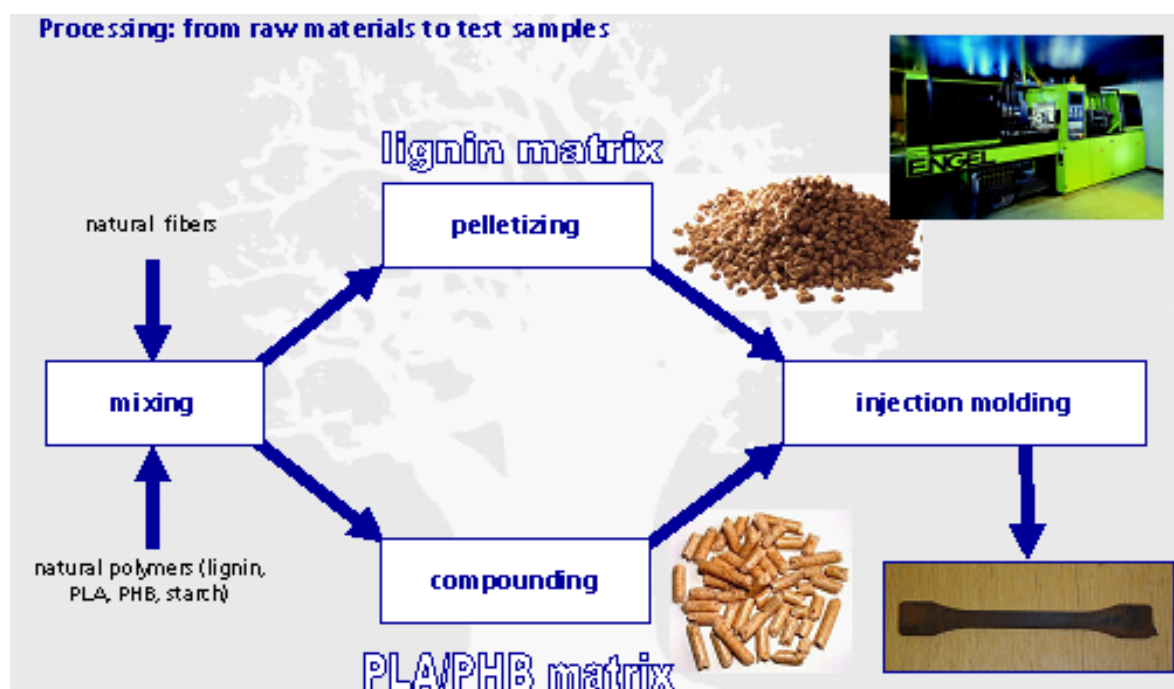


Figure 5: Thermoplastics processing by mixing, compounding/pelletizing and injection moulding

5.1.1 Lignin matrix composites

Lignin is one of the most abundant organic molecules on earth covering between 25-30% of the non-fossil organic carbon in various biomasses. Three basic monolignols, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol form a complex 3-dimensional structure (see Figure 6).

Worldwide, chemical pulp mills generate approximately 50 million tons every year as a bi-product of the pulp and paper industrial processes. Starting with activities more than 10 years ago a material evolved which consists of lignin, natural fibers for reinforcement and natural additives fulfilling criteria with regard of processing and performance and especially those of Biocomp.

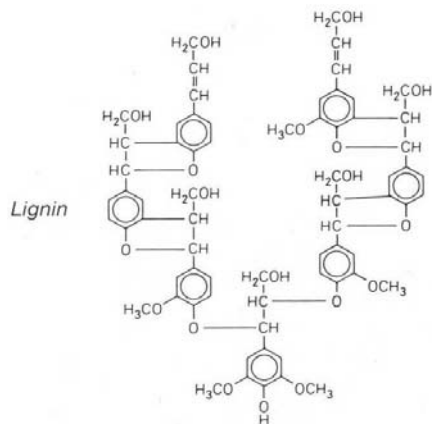


Figure 6: Structural element of lignin

Exhibiting wood-like properties, lignin formulations can be processed like a thermoplastic material. It shows the potential for manufacturing industrially relevant products. The mechanical properties of the material depend on the fiber content (Figure 7). The material developed in the project, experienced

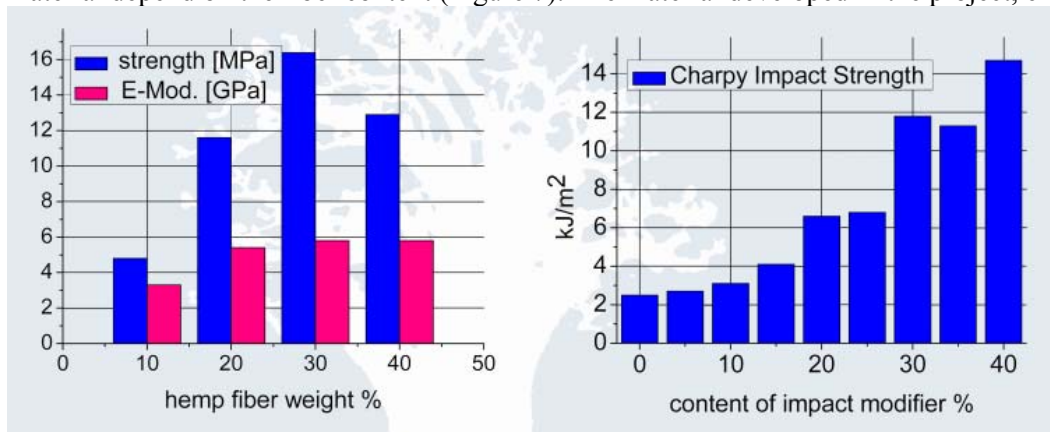


Figure 7: Elastic modulus and maximum tensile strength of materials with hemp fibers depending on the fiber content (left) and the impact strength (right)

a substantial progress of the impact strength to enable applications similar to those of polypropylene/talcum and of low quality polyamides. The excellent acoustic properties proved by dynamical frequency dependent testing predestinate this material for loudspeaker housings. A mould was designed and constructed to manufacture such covers in a single step. Without sink-marks in the 1cm thick shell of a 250mm diameter, a perfect dimensional stability resulted from the trials. Figure 8 illustrates the tools on the injection moulding machine and the completed loudspeaker.



Figure 8: Mould for a spherical loudspeaker cover with wall thickness of 10mm and a diameter of 250mm and the surface finished completed box

5.1.2 Starch based materials

The hydrophilicity of the starch is a major barrier to prevent its large scale industrial use. However this was reduced in Biocomp by crosslinking of the native starch hydroxyl functionalities and substitution of the hydroxyl functionalities with for example acetyl groups. When more than two thirds of the available hydroxyl functionalities in the starch molecule are substituted, the intra- and intermolecular hydrogen bonding is reduced sufficiently to significantly lower the T_g (glass transition temperature) and render the material melt processable. To further bring down the T_g , the material is typically plasticised either externally by triacetine (Triac) or triethyl citrate (TEC), for example or internally using hydrophobic substitutive groups instead of acetyl groups in the initial substitution reaction. The plasticised starch acetate compound (PSA) uses a range of natural fibers: hemp, flax, and wood fibres in weight % of 10-60 and applies the processing schemes for preparation of the starch composites (Figure 9). An optimized formulation with a 40% flax fiber content resulted in the following mechanical properties: tensile strength 50.7 MPa; E-modulus 8054 MPa and impact strength 5.2kJ/m². The temperature stability should still be improved.

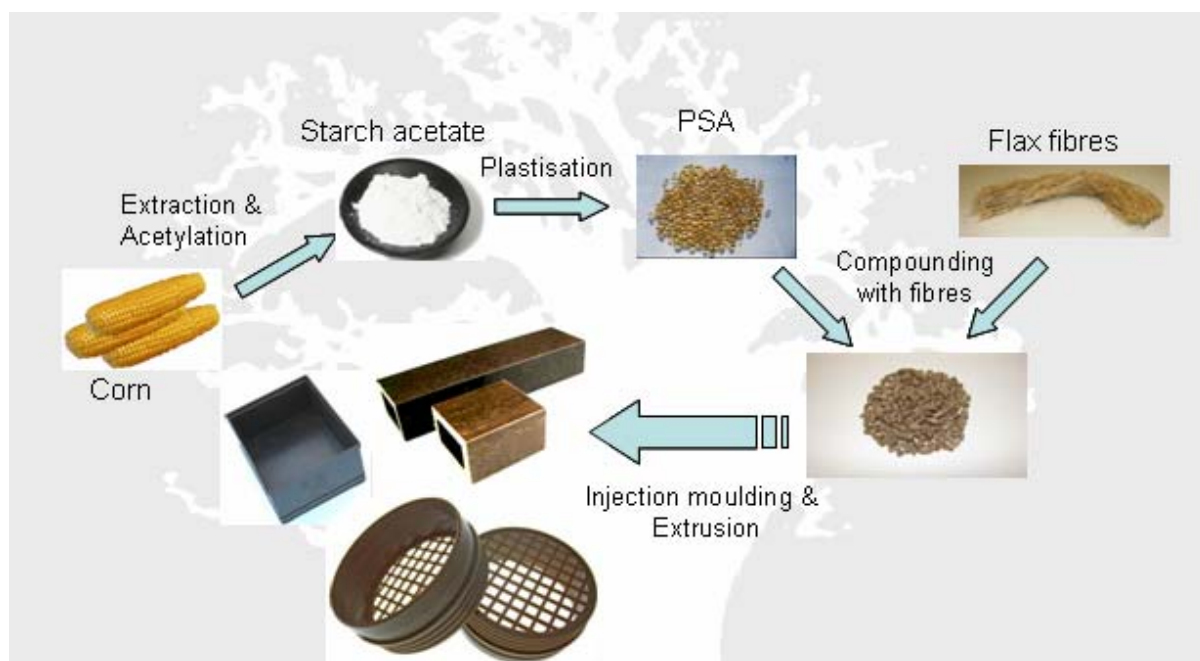


Figure 9: The manufacturing chain for starch natural fibre compounds and samples by injection moulding (thin walled boxes and respirator casings) and by extrusion (rectangular profile). Outer dimensions of boxes in (mm): 65 x 100 x 120 and the casings 25 x 63 (Ø).

5.1.3 PLA matrix composites

Poly lactide (PLA) is a biodegradable, aliphatic polymer, which can be obtained from renewable resources by fermentation and is mainly used in medical applications. Nowadays PLA is entering the packaging market due to its good barrier properties. Natural fiber filled PLA compounds show enhanced mechanical properties e.g. stiffness, but toughness still needs to be increased. Impact modification solutions gained in Biocomp enable engineering applications with good mechanical properties including a tensile strength of 46MPa, an E-modulus of 4400MPa, an impact strength of 29.4kJ/m² and a temperature stability (HDT) above 100°C (PLA HM1010, 10% flax, 10% impact modifier). Approaches to modeling the mechanical behavior were successful, enabling structural (Figure 10) and flow field simulations (Figure 11). The latter requires large data sets, the viscosity, important for flow simulation in injection moulding, is shown in Figure 11.

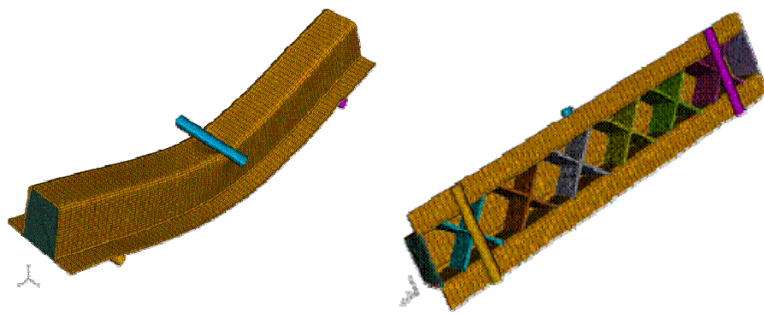


Figure 10: Structural simulations of a generic structural profile with honeycomb structure

A generic structural beam was analysed using an FEM code as plotted in Figure 12 in order to optimize bending stability and to compare with experimental testing. After planning the structure, the tool design has to be based also on a flow simulation (moldflow®) which needs various input parameters, especially the viscosity as shown for the material in Figure 11.

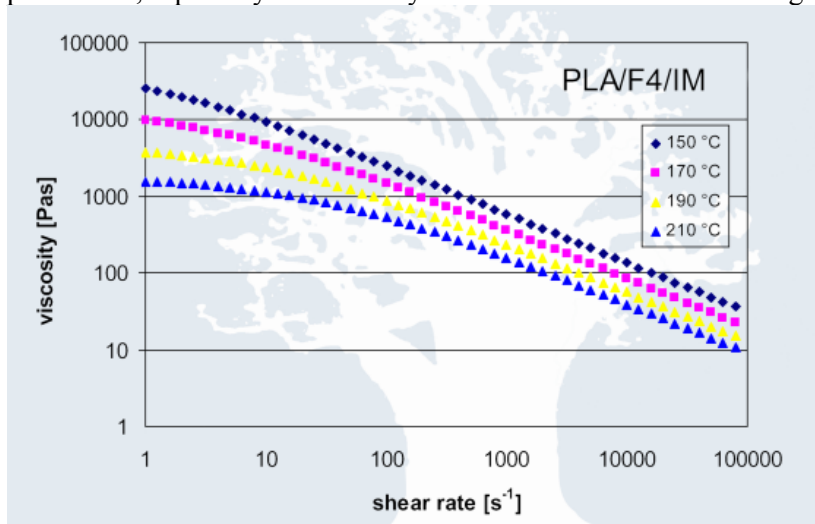


Figure 11: Flow curve (viscosity) of the PLA/Flax/Impact modifier grade

Figure 12 depicts a plot from the flow simulation and a picture of injection moulded parts. The results indicated the applicability of computer simulation, which is widely used for synthetic plastics, also for PLA matrix composites.

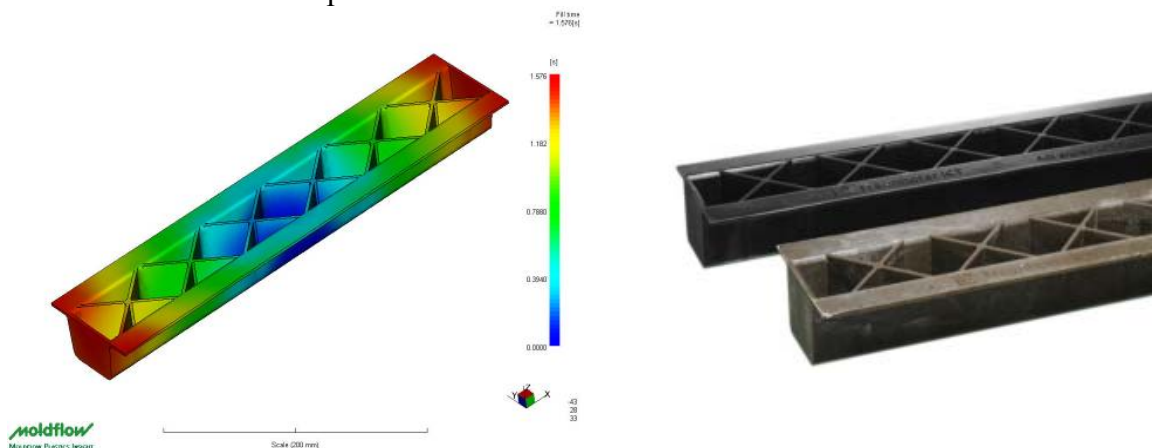


Figure 12: Moldflow simulation of the structural beam based on measured data especially viscosity (left) and the injection moulded parts (right)

Adequate evaluation of properties includes flexural testing, in Figure 13 a beam made from the PLA matrix composite (20% flax fibers) with comparisons to a benchmark polypropylene material (glass fiber 20%).



Figure 13: Bending tests and broken beam

Table 4 contains the data corresponding to failure on the bending test. Still there is a brittle failure of the Biocomp materials, however stiffness and maximum load are more than twice that of the glass fiber reference sample, a finding which highlights the performance.

Table 4: Data of failure

	PLA 20%Flax	PP 20%Glass
Failure behaviour	Brittle	Ductile
Maximum load on failure	2880±270 N	1327±22 N
Deflection at maximum load	10.8±1.5 mm	19.1±0.8 mm
Stiffness	433.1±18.5 N/mm	191.2±4.1 N/mm

A pre-selection of a material for frames for eye glasses favors a PLA type material. Preselection based on thermal stability indicates lignin, starch and PLA as the most appropriate materials; preselection based on aesthetics indicates PLA and lignin; preselection based on flammability indicates PLA; and the tensile test and assembling again indicates PLA. The requirements for mechanical stability challenge Biocomp materials to their limits. However, a PLA material (PLA V1C) with impact modifier (< 80 kJ/m²) comes close to a solution. Trials were made with available tools and the results are shown in Figure 14:



Figure 14: Eye glasses frames in comparison of an impact modified PLA with PA 12 and a testing equipment

An evaluation of all relevant tests is listed in Table 5. The selected PLA material of Biocomp fulfills the criteria but with some drawbacks mainly related to the thermal stability.

Table 5: Material evaluation after various test, which a PLA material nearly fulfills

Material	PLA	Starch	Lignin
<i>Mechanical performance</i>	√ / X	-	-
<i>Thermal stability</i>	√ / X	√	√
<i>Ignition</i>	√	-	-
<i>Aesthetics</i>	√	X	X
<i>Assembling</i>	√ / X	-	-

5.1.4 Advanced processing

LFT-D-ILC

Biocomp initiated the use of innovative processing methods to manufacture materials and semi-finished parts. A process, very cost effective and reducing thermal loads to the components, is the long fiber technology by direct processing and in-line compounding (LFT-D-ILC), which is currently applied for glass fiber reinforced thermoplastics in industry. This method was modified to develop a demonstrator - a foot rest fitting for a car (Smart) - comparing all basic fiber types hemp (cut slivers, 2-5mm), flax (cut slivers, 2-5mm) and wood together with PLA and impact modifiers (see Figure 15). This technology achieves high mechanical properties without reduction of impact strength. Reinforcement of PLA with cellulose regenerated fibers (CRF, 20%) led to an impact strength to surpass 50 kJ/m², the Young's modulus still above 5000 MPa. This is considered a very successful result from the project.

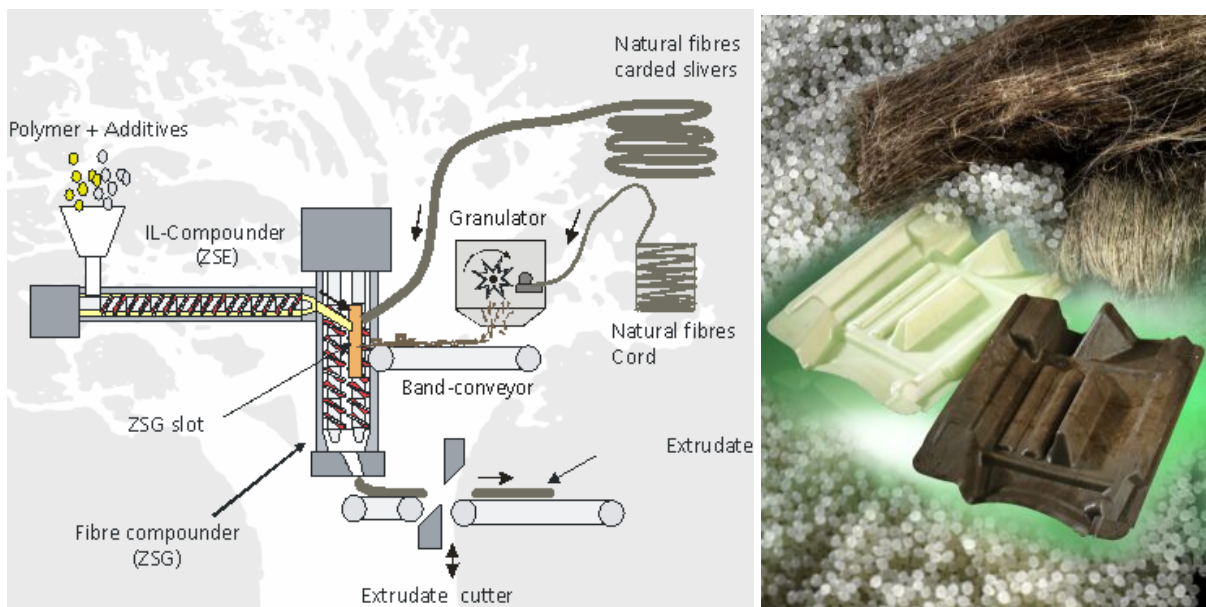


Figure 15: Innovative processing by the single step processing of long fiber technology direct processing and in-line compounding (LFT-D-ILC), footrests for an automotive application were manufactured.

Compounding by a planet screw extruder

Dispersion of the fibers in the matrix and reduction of thermal loads to the composite constituents are crucial issues for high quality Biocomp materials. A planet extruder with 1 center screw and e.g. 8 planet screws around the center screw meets these requirements and provides a homogeneous fiber dispersion/distribution, a very good degassing and “soft” compounding conditions. The avoidance of thermal peaks limits thermal damage of matrix and fibers thus conserving mechanical properties. The compounding of PLA based materials with plasticising additives achieved a quality acceptable for the glasses frames of Figure 18 with the impact strength above 80 kJ/m². Figure 16 shows the production of impact modified, natural fiber reinforced PLA granules on a planet screw extruder.



Figure 16: Compounds manufactured by the planet screw extruder

Conical extrusion

PLA matrix composites can also be extruded in a similar way like wood plastic composites WPC (with synthetic polypropylene). 5 Biocomp materials were extruded to profiles with a Conical Twin Screw Extruder- Cincinnati T58 fiberex with the compositions of PLA 30%Hemp and impact modifier, PLA 50%Flax, TPS (thermoplastic acetylated starch) 50% Hemp, PLA 30%Wood and PLA 50%Wood.



Figure 17: Bending test of extruded beams from PLA and natural fibers

The bending tests (Figure 17) led to the following results comparing the different materials used:

- Very good reproducibility of results between samples
- PLA 50%Wood demonstrated the higher stiffness while TPS 50%Hemp the lower
- All other three materials showed very similar values of stiffness
- PLA 50%Flax and TPS 50%Hemp had no catastrophic failure at the end of the test
- PLA 30%Hemp-3IM, PLA 30% Wood and PLA 50% Wood failed catastrophically

In addition, a conical extruder from Conenor was applied processing 50% flax fibers with plasticised starch acetate to a rectangular beam (Figure 9)

Film stacking

Vacuum consolidation and press moulding of PLA film stacked with various natural fibre materials included non-woven flax, woven hemp and unidirectional flax fabrics. For vacuum consolidation, the PLA film and natural fiber materials were stacked alternately to obtain the desired thickness and percentage fiber, placed on an aluminium tooling plate, covered with release film, breather cloth and a vacuum bag, which was sealed with sealant tape. For press moulding, the same procedure occurred in a heated press, pressed at 5 bar, heated to the target temperature (160-200°C), held for 5 minutes and then water cooled whilst maintaining pressure. Tensile test resulted in Young's moduli of 8000-10000MPa and strengths between 114 to 127.5MPa. Both vacuum consolidation and press moulding are viable processes for PLA-natural fibre composite parts. Non-woven flax mat and unidirectional stitched flax fabric provide suitable reinforcements. In general, tensile modulus and strength increase with increasing fibre content – for vacuum consolidation, the optimum fibre content for unidirectional flax is 40wt% and for non-woven flax is 20wt%. Shorter times at temperature minimize thermal degradation of natural fibres and result in better properties - for vacuum consolidation, the optimum process is 190°C for 10 minutes.

Measurement of the fiber content on compounding by extrusion

When extending the manufacturing of Biocomposites to industrial scale the advanced technologies of plastics for quality control have also be implemented into the processing. Biocomp showed that natural fiber reinforced biopolymers allow the direct measurement of the fiber content, because the cellulosic fibers absorb light in the Near Infrared Spectral region. However, a statistical data evaluation (Principal Component Analysis, Multivariate Curve Resolution) and its use for calibration is needed. A calibration transfer is possible between 2 extruders with results as presented in Figure 18. Calibration was elaborated at a lab-scale extruder and successfully implemented at a small production extruder and enables the application of NIRS to production without delay.

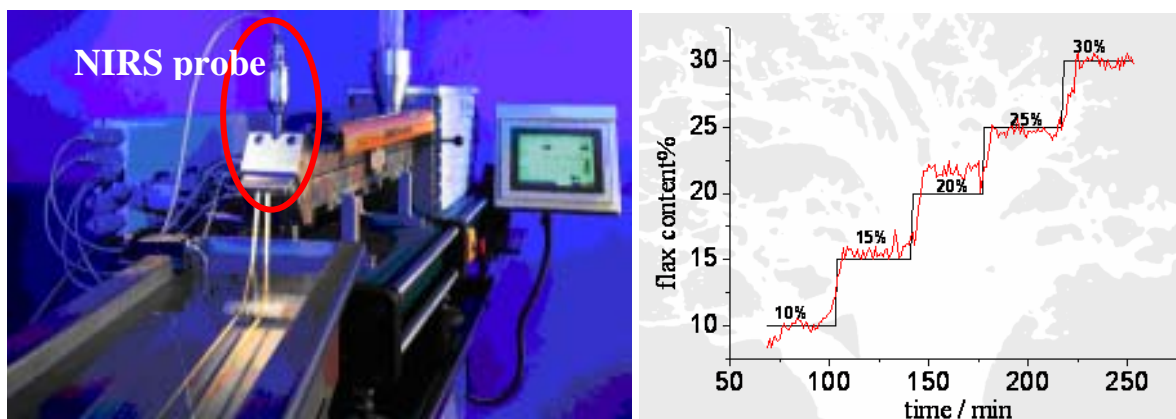


Figure 18: Flax content measured at UAR extruder predicted by Fh-ICT calibration model

5.2 Thermosets

For thermoset materials furan resins and plant oil resins were selected from various polymers. The potential of the furan to achieve properties of synthetic thermoset composites was estimated to be high with benefits of high thermal and chemical stability, whereas as the crops oil derivatives would be free of formaldehyde.

5.2.1 Furan resins

Furfural a precursor for furan resins emerges from further processing of polysaccharide hemicellulose constituents by digestion and dehydration. The preferred biomass is bagasse a residue from sugar cane.

A straightforward hydrogenation produces furfuryl alcohol which reacts with acidic curing agents to a resin of oligomers and/or polymers (see Figure 19).

The state of the art applications before Biocomp concern low grade resins for the foundry industry and special ones for chemical resistant parts. The Biocomp objective was to establish the furan resins as standard plastics resins, includes also the screening of important processing methods and to obtain related oligomer compositions to meet requirements of temperature, pressure and curing time. A rapid progress in the project brought already some methods to a mature state of near term industrial use. The production of the resin reached pilot scale. The demonstrating parts were of a remarkable size of 1 to some meters.

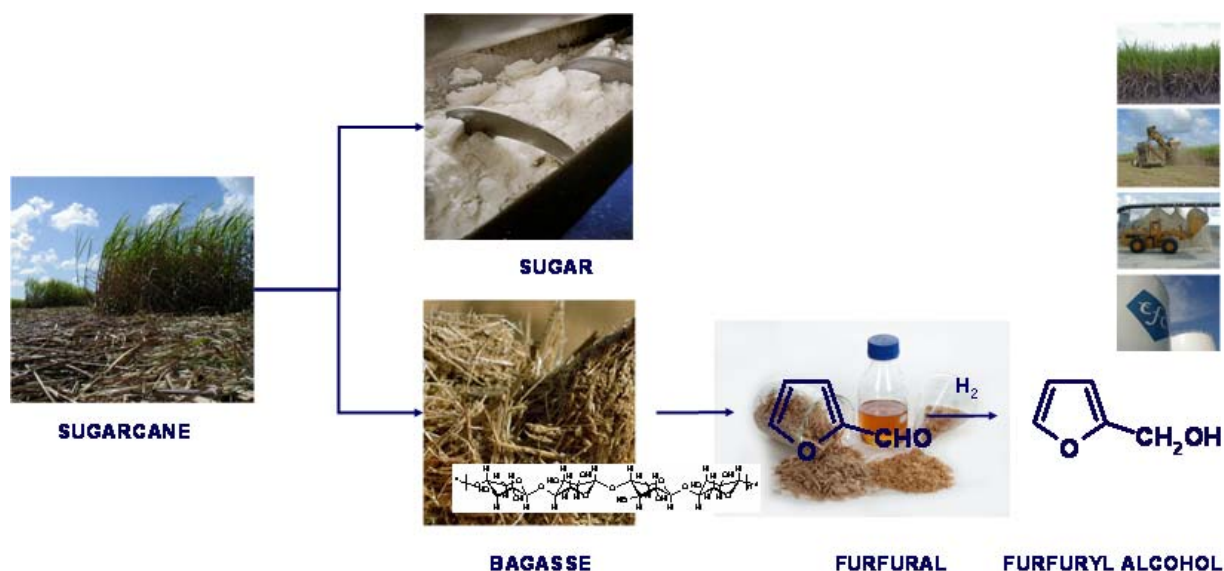


Figure 19: scheme of the reaction of hemicellulose components to furan resins

Two types of resins Biorez® and Furalite® were prepared. Each exists in various modifications. Using water, the viscosity can be modified between 10000 and 200 cps. Compression moulding of mats with the resin sprayed up could reach a prototype status. Figure 20 illustrates the process and a resulting part, an automotive door panel.

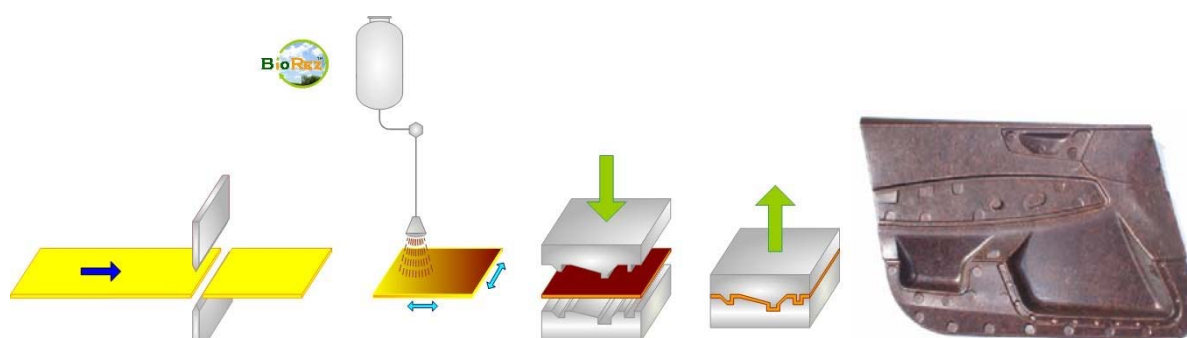


Figure 20: Hot compression moulding of non-woven fiber mats sprayed with a one component resin: the process scheme, the achieved scale of demonstrator manufacturing of an automotive panel

Automotive applications arise already by the potential of substitution synthetic resins in door panels by a one component Biorez formulation. Table 6 lists important data, which demonstrate the surpassing of the relevant specifications.

Table 6: Data of the compression moulded automotive door trim

Density [g/cm ³]	Flexural modulus [N/mm ²]	Flexural strength [N/mm ²]	Impact strength [kJ/m ²]	VOC [µg/g]
0.8 – 0.85	3000 - 5000	50 - 90	>30	< 30

Prepreg technology

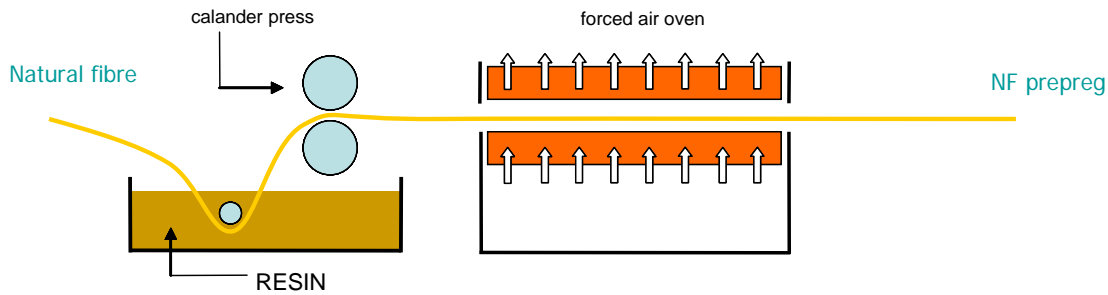


Figure 21: Production of NF-furan prepreg by textile impregnation

Prepregs arise from impregnation of fabrics or non-wovens by a resin which is only partially cured. They are typically consolidated and moulded into parts by vacuum, autoclave or press moulding, depending on the part size and shape, production volume and quality required. Vacuum consolidation stands for the process with the lowest investment cost in terms of tooling and equipment, so it is preferred for large, low volume parts. However, higher pressure processes often provide higher quality parts. Figure 21 illustrates the principles of the process.

A model product panel (ambulance panel) from a low-volume utility vehicle was used to demonstrate and evaluate the materials against a specification. Typical requirements for this type of component include mechanical integrity, impact resistance, environmental resistance, good surface finish, acceptable cost at low production volumes (e.g. 200/year). These properties were measured all with values which demonstrate the targeted application. For modelling a 3-dimensional model was created in ABAQUS software code using 2nd order reduced integration elements were used (C3D20R). The materials modelled were: GRP (glass fibre chopped strand mat/polyester resin) was modelled as isotropic linear elastic material - $E = 10.6 \text{ GPa}$ and $\nu = 0.35$ as measured and BIOCOMP1 (glass fibre chopped strand mat/Biorez 050915) was also modelled as isotropic linear elastic material $E = 6.9 \text{ GPa}$ and $\nu = 0.35$ as measured in Biocomp. The load cases represented the panel being opened with both catches accidentally locked, one catch accidentally locked and also the effect of thermal expansion contraction in temperature extremes. The model is illustrated in Figure 22. The relevant stresses for these different loading cases were compared for the two materials.

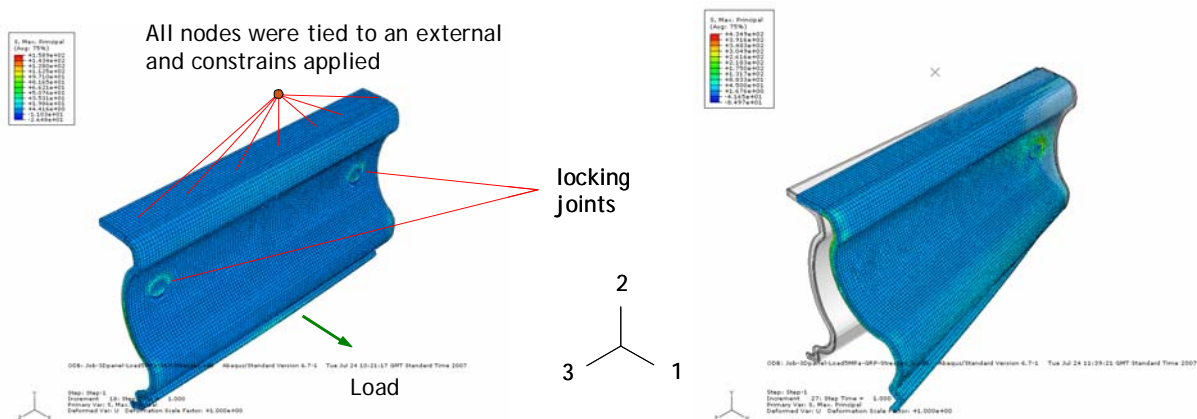


Figure 22: Structural modelling of the ambulance panel on load

A coupled temperature – displacement model was used for the thermal analysis using 1st order coupled temp-disp 3D elements were used (C3D8T). The CTE of the materials were measured experimentally and used in the model (GRP 30 $\mu\epsilon/^\circ\text{C}$ and BIOCOMP1 20 $\mu\epsilon/^\circ\text{C}$). A temperature gradient of 55 $^\circ\text{C}$ was applied representing the possible swings in temperature with different climates. All degrees of freedom were constrained for the upper edge of the panel. Strains were extracted from the model at specific locations which would later be measured using strain gauges on the panels. Here, because the BIOCOMP panel has a lower CTE, the strains are lower than in the GRP panel and hence will have lower tendency to bind or stick. Real testing of samples could confirm the results of simulations.

Vacuum consolidation

Layers of the prepregs were placed on a PTFE-coated aluminium tool/plate, covered with release film, breather cloth and vacuum bag, a vacuum of 0.95bar was applied, the whole assembly was placed in an oven and heated to the target temperature (typically 150 $^\circ\text{C}$), held for a given time (typically 15 minutes) and cooled whilst maintaining vacuum pressure. A thermocouple recorded the temperature of the prepreg laminate to achieve sound panels with properties listed in Table 7.

Table 7: Mechanical properties of prepreg materials

Material	Flexural modulus [GPa]	Flexural strength [MPa]	Fiber content [vol%]
Furan / Engtex KOM784 flax cross ply	9.6	99.4	41
Furan / glass plain weave	9.0	104.6	57
Furan / carbon twill weave	26.2	364.7	42

With resins to be cured at lower temperatures larger devices were manufactured by vacuum infusion, an example is show in Figure 23.



Figure 23: vacuum infusion to manufacture a boat

In addition, sandwich panels were prepared by placing balsa or synthetic plastic foams between 2 furan skins (Figure 24) based on the prepreg technology.



Figure 24: Sandwich panel Failure type and locus for the furan/balsa sandwich

The force – deflection curve of the sandwich panel together with a synthetic reference material (polyester /glass fiber composite) and its stiffness were measured. The stiffness of the bio-composite material is 186% higher than the polyester/glass fiber composite. There was some considerable scatter in the measured flexural strength of the bi-composite, but even the lower measured value is higher than that of the reference material.

The following conclusions have been drawn for prepreg materials (advantages and drawbacks):

- The furan prepreg system is suitable for producing high-performance composites with glass and, more importantly, natural fibres.
- The prepreg can be moulded by vacuum consolidation or press moulding.
- During vacuum consolidation, the resin bleeds out leading to significant porosity.
- Surface finish can be improved by using surface veils or heated tools.
- During press moulding, it is necessary to allow steam to escape periodically to prevent blistering and delamination.
- The prepreg can be used to make a variety of shaped parts including sandwich panels, tubes and panels, although the drape and tack is not ideal.
- The stability of the prepreg against acidity of the resin could be demonstrated for pH-values above 3 a requirement the relevant resin types meet.

BMC: Bulk Moulded Compound



Figure 25: BMC processed to trays by hot compression

Bulk moulding compounds (BMC) consist of short fibers impregnated with a furan resin including functional additives to be compression or injection moulded. The process enables short manufacturing cycles. Table 8 lists important data concerning the developed materials. Impact strength has still to be improved, however many applications in various industries can be covered by the developed process. The temperature stability and flame resistance are remarkable.

Table 8: Data of BMC materials

Property	Units	Standard	Glassfibre based BMC	Flaxfibre based BMC
<i>Physical properties</i>				
- Fibre content	wt%	-	10- 18	10- 11
- Density	g/cc	UNE 53020	1.7 – 2.0	~ 1.7
<i>Thermal properties</i>				
- Deflection temperature at 1.8 MPa (HDT)	°C	ISO 75-1 / ISO 75-3	> 100°C	> 100°C
<i>Mechanical performance</i>				
- Flexural yield strength	MPa	ISO 14125	50- 70	45- 55
- Flexural modulus	MPa	ISO14125	8,500 – 11,500	8,000 – 10,000
- Charpy impact strength	J/m ²	UNE 53021 / ISO 179-1	3,000 – 4,500	~ 1,000

SMC: Sheet Moulded Compound

The SMC-process is an important standard process technology for fibre reinforced polymers for industrial production. The key issue concerns the flow behaviour of the semi-finished flat SMC-sheet under heat and pressure in a press-flow-forming technique. The SMC-sheet emerges continuously from short fibers or endless mats impregnated with the furan resin formulations and ends with conditioning to complete curing. Final SMC processing of the resins was successful by an adequate chemical thickening and curing enhancement of furan based resins by balancing the catalyst with the acidity (pH-value) to get the process to run stably. Real scale trials are shown in Figure 26.



Figure 26: SMC process and solving important problems of thickening and catalyst balance

Hand lay-up

An **unmanned aerial vehicle (UAV)** application requires light weight structures which are subjected to extreme aerodynamic loads. A Mini-UAV was designed and manufactured by a hand lay-up procedure, using a furan resin together with natural fibres, as well as carbon fibres for reinforcement and for comparison glass fibres. The used tools consist of two parts for an upper and lower side of the UAV. The area of each tool is approximately 0.27 m² built of an epoxy resin (0.75g/cm³). The materials are:

- **Resin:** two component system TransFurans Biorez 050915 (740cps viscosity), S-type-catalyst (50% H₂O)
- **Natural fibres:** KOM 783 (Flax/Cotton) 173 g/cm² and H 18 (Hemp) 195 g/cm² fabrics
- **Carbon fibres:** Aero 93 g/m² and Atlas 120 g/m² fabrics.

The lamination occurred by applying the resin, fibres and tooling plate at room temperature and working the resin into fibres using a brush. Curing took place as follows: a vacuum was applied for 2.5h at room temperature, vacuum was removed, laminate was placed into an oven at 50°C for 2h, then heated up to 80°C and held for 18h, the laminates were cooled in the oven to room temperature.



Figure 27: Processing the natural fiber reinforced Mini UAV

For the lamination of the natural fibres 3 layers were used in different directions. Bottom: H 18 1st layer: 60.5 g/m² at 90°, 2nd layer: 60.5 g/m² at +45°, 3rd layer: 60.5 g/m² at -45°, Top: KOM 783, 1st layer: 173 g/m² at 90°, 2nd layer: 173 g/m² at +45°, 3rd layer: 173 g/m² at -45°. The total amount of resin used for the bottom part was 356g while for the top part it was 552g. For the lamination of the

carbon fibres 650g of resin were used and there were laid up two layers as follows: Bottom and Top 1st layer: 93 g/m² at +45°, 2nd layer: 120 g/m² at 0°. Flat sheets were investigated for achieving the mechanical performance of the composites. The results show good consistency in terms of measured strength and modulus for samples in both direction of cutting. The samples of both reinforcement fibres showed evidence of delamination, as illustrated clearly in Figure 28. The delamination of the specimens under the tensile load is due to the different fibre directions in two or three layers that comprise the samples. Due to this asymmetry in the lay-up, the applied tensile loading leads to large shear stress at the interface of the layers. Table 9 lists the averaged results for the composites.



Figure 28: Failed (a) carbon fibre reinforced and (b) glass fibre reinforced Biorez samples

The Young's modulus of the carbon fiber materials is essentially higher and the tensile strength similar within the experimental errors, considering that there are only 2 layers compared to 3 layers and a lower weight of each layer.

Table 9: Mechanical properties of the hand lay-up furan matrix composites

Plate	Direction	Strength [MPa]	Strain at Break [%]	Modulus [GPa]
Carbon fiber: A	Horizontal	242.2±20.8	0.99±0.10	25.1±0.9
	Vertical	262.2±29.5	1.17±0.09	24.0±1.0
Glass fiber: AA	Horizontal	235.6±13.8	1.78±0.12	16.2±0.6
	Vertical	274.8±12.1	1.84±0.20	18.2±0.7

The furan resin matrix composites achieved a mature stage of development which will rise a considerable attention to the material. The carbon fiber reinforced material version show promising properties with respect to strength, temperature stability and fire resistance.

5.2.2 Crops oil derived resins

The target of the project was the development of **formaldehyde-free** bio-based composites, using natural fibers and crop-oil derived binders. The composites are to be used as insulating, sound-absorbing and structural or semi-structural materials. The medium-density fiberboard (MDF) is a typical example of such materials. The main starting materials for binders were modified vegetable oils, especially **maleinised and epoxidised oils**. The main fibres used were wood, hemp and flax fibres. As in MDF commercial products, a the processed fiber boards used a high proportion of natural fibre was used, namely about 75-80%. Composite panels were manufactured by hot-pressing of the mixture of the components. They were tested according to current standards, and the finalized panels fulfill the related criteria. A typical example of manufacturing conditions, along with test results, is shown below (Table 10).

Table 10: Conditions of resin processing

Compounding time, minutes	Fitting time in stamper	Pressing temp., °C	Pressing time, [min]	Conditioning, [min]	Total time [min]	Thickness [mm]
5 in three steps	3	122/160 2 steps	29	60	1h37.	6.16

The research effort resulted in obtaining composite products with increased stiffness, increased internal cohesion, good resistance to water, low level of odour, flame-retardant properties (by incorporation of adequate agents). **Eco-friendly demonstration objects**, namely **a model door, a full-size door and a full-size night table** were manufactured by bio-based panels as structural (MDF) and insulating (LDF) elements (Figure 29).



Figure 29: Eco-doors as made from formaldehyde-free fiberboards with crops-oil based binders

5.2.3 Curing kinetics by Near Infrared Spectroscopy

In-/On-line measurement of the curing of resins by Near Infrared Spectroscopy provides precise information on the curing reaction in-situ of the process. The NIR spectra show the decrease of OH (alcohol) functional groups and the growths of CH bonds, as well as they indicate water indicating its generation and diffusion on reactions. By a multivariate evaluation an initial “reactant” and a “final product” could be identified and quantified for furan resin curing. The curing kinetics of the resins and prepreps could be described including analysing curves of thermal analysis DSC, and DSC in parallel to NIRS assuming autocatalytic reaction models.

5.3 LCA/LCI of Biocomp materials

Evaluating Biocomp, Live Cycle Assessment (LCI/LCA) focused onto resin processing, the energy consumption and effects to the climate change as well as on further materials and additional impact categories. It used Biocomp processing results as summarized in the chapters above, mainly for PLA, furan and lignin based composites, respectively. A comprehensive literature review revealed a number of LCA studies performed on hemp and flax fibers e.g. furfuryl alcohol, PLA and other matrix materials e.g. as well as a number of more general studies. The functional units considered were the “Risø-bowl” made of PLA/hemp, glass fiber/polypropylene (GF/PP, TWINTEX) and furan resin/

hemp prepreps using compression moulding. Both, synthetic polymer composites and biocomposites may be produced using the same processing conditions and thus the same energy demands. In other processes the biocomposites needed e.g. lower temperatures and therefore a lower energy consumption to produce the product. Additionally, the “thin walled box” made of PLA and PP and the processing of the (generic) bathroom floor were analysed due to the non renewable energy consumption. The following aspects of natural fibers and matrices regarding the sustainability were identified:

- Hemp seems to be the better alternative compared to flax with regard to pesticide use for weed control and agricultural benefits.
- Flax produces fibres and seed (sowing, oil extraction, animal feed)
- Dessication with Glyphosate may be adopted in certain cases for hemp (baby –hemp approach) and flax. (Glyphosate is though frequently used e.g. in corn production (PLA), but according to the literature the pure substance is much less ecotoxic than other pesticides- though effects are found for formulations). Nevertheless, the industrial quality of the fibres resulting from that process is diverting very much being presumably not the best methodology for high quality industrial grade fibre production.
- Comparing different retting scenarios hemp and flax have about the same impact.
- Furfural the precursor of furan resins is processed from a variety of agricultural waste products.
- Overall LCA score for processing furan oligomers is dominated by the emissions from old-fashioned primary process equipment ”own by Quaker Oats” and ”Chinese method” – new approaches promise substantial improvement.
- Lignin is produced also from “waste” products coming from pulp industries or bio-ethanol processing. The overall score is better than for crude oil based matrix materials.
- PLA biotechnological production avoids highly toxic educts (hydrogen cyanide).
- PLA: Gen modification may improve the sustainability of PLA production

Sustainability of industrial biomass production and their industrial utilization will depend on three sustainability pillars environment, economy, social. Thus the value orientation according to weak or strong sustainability has therefore always to be reflected versus:

- reference scenarios and alternatives in a holistic approach
- demand of biomass: increasing due to growth in wealth and population
- supply: competition with alternative biomass uses – price relations with fossil energy affect both demand and supply
- complementary and complete use of all constituents in regionally balanced approaches: food, materials and energy
- certification systems can be made – control of displacement ?
- Many sources of exergy available other than those based on photosynthesis – leave primary biomass for food, feed and fiber (-fuel)

Summarizing, Biocomp processes revealed the promising sustainable potential of the biomaterials used for industrial composite manufacturing. The main impact seems to be within the agricultural and pre-processing of the different components of the composites. The manufacturing of the biocomposites is assumed to be comparable to the processing of the common composites with a tendency to e.g. less energy usage for the biocomposites. The matrix materials furan resins and lignin are produced from agricultural or process waste products. Therefore, the usage of these will not address the resource depletion issue or be subject of the discussions on the competition between plants being used as food or materials. Nevertheless, the utilization of biomass for production of process energy – not proposed by Biocomp - is questionable, the use for materials seems to be more effective, as an energetic use is obviously possible at the end of life. However, a continued improvement of processes, especially concerning the introduction of cleaner and more effective technologies should be prioritized in the future developments. E.g. as mentioned for the furfural production, a number of newer and more effective technologies are available or under development.

5.4 Conclusion on materials evaluation by demonstrators

Biocomp made a substantial progress in the development of materials from renewable resources and their knowledge-based processing. Manufactured and tested demonstrators could reveal the quality of the materials, the data of selected formulations are available in data bases.

All 4 thermoplastic matrices with natural fibers can be processed to plastic or wood-like materials and parts of engineering quality for industrial mass production. The materials exhibit technical advantages, but although they still have to overcome drawbacks (Table 11), they can compete with synthetic plastics.

Table 11: Technical advantages and drawbacks of thermoplastics

Composites with natural fibers	Lignin	Starch	PLA	PHB
Strength	0	0	++	0
Stiffness	+	+	+	0
Impact strength	0	0	++	+
HDT	+	0	-	-
Reproducibility	0	+	++	+
Fire-proof	++	0	+	-
Acoustics	++	+	+	+
Visual appearance	++	0	+	0
Dimensional stability	++	0	+	0
Emissions / odour	0	0	+	+

New thermosets starting from a very rudimentary status proved to promise highly competitive composites for industrial manufacturing. The main related standard processing methods work with these furan resins and plant oil resin (wood fiber boards). For furan resins prepreg technology, hand lay-up, vacuum infusion and spray-up/hot compression can enter industrial development in basic applications. BMC and SMC development needs further RTD efforts (see Table 12).

Table 12: Successful developments and progress still required for thermosets

Material	Production	Mechanical characterisation	Comparative material	Performance in use
NF-furan (spray up – hot compression moulding)	√	√	NF-PU NF-EP	√
NF-Furan (NF prepreg)	√	√	Glass- Polyester Glass-furan	√ (partially)
Glass-furan (vacuum infusion)	√	√	Glass- Polyester Glass-furan	√
Glass/NF-furan (BMC-SMC)	√	(partially)	Glass- Polyester Glass-furan	To do

NF – natural fiber, prepreg – pre-impregnated fabrics, PU - polyurethane, EP - Epoxy resin

6 Roadmap

The promising results of Biocomp concern a broad range of bio-polymers and natural fiber reinforcement approaches which can be used in industrial mass production of semi-finished and finished parts. At the start of the project, the main standard processes were investigated to address a limited number of functionalities of the composites. Flame retardancy and increased impact strength led to substantial steps forward. The properties should be designable, in the same way that synthetic plastics offer a formulation for each individual requirement. Testing and material models were screened and the results demonstrated that adequate modeling is possible. The results also revealed particular effects which required an innovative approach. Although spectroscopic in-line control was not found to be more important in the new processes than in its current use, it had some advantages where used in the processing of biocomposites. It sped up developments and supported especially the understanding of curing kinetics for thermosets. As separately handled in Biocomp the following issues should be considered for future R&D:

- Biopolymers:
 - New or re-invented old biopolymers from biorefinery processes: tannin, furfural based, hemicellulose constituents, macromolecules synthesised from breakdown compounds of cellulose and lignin (e.g. polyamides or polyurethanes)
 - Formaldehyde free resins based on plant oil derivatives by various chemical modifications (maleinising, exopidising etc.)
 - Progressed commercially available thermoplastics for which a considerable progress was achieved: **lignin, starch, polylactide (PLA) and polyhydroxybutyrate (PHB)** are bio-technology derived, to improve impact strength, thermal stability, glass transition points, crystallinity, sensitivity against environmental stresses/humidity, screening of pre-treatment like annealing, blending of different modifications and
 - Thermosets: Innovative **Furan resins** modified to achieve properties far beyond the current state of the art, new plasticizer, modifiers for adjusting viscosity, catalysts for the different standard processes and temperature ranges.
 - **Plant oil resins**, formaldehyde free, could be derived by various types of chemical modification of oils from second generation biomass (residues), increase temperature stability, viscosity, plasticizers, use of new curing catalysts.
- Natural fibres:
 - Enlarge the fibers to world-wide grown loose fibers and slivers with their broad spectrum of properties of elasticity, surface, fineness and mechanical properties for thermoplastics and
 - Loose fibers, non-woven mats and woven fabrics for thermosets of different origin
 - Extending pretreatment: acetylation, bleaching, plasma-treatment, impregnation with oligomers and resins, precipitation of additives of various nature
 - Support feeding: by cutting, transporting, palletizing with innovative methods
- Additives natural or eco-friendly for:
 - Flame retardants to meet highest criteria for transport (extend findings in Biocomp)
 - Plasticisers and impact modifiers (extend findings in Biocomp)
 - UV-stability, electrical, thermal conductivity, dyeing, reduce emissions and others to achieve all relevant functionalities of synthetic plastics
- Design/simulation:
 - Enlarge investigation in control methods in pre-treatment, processing and quality assurance

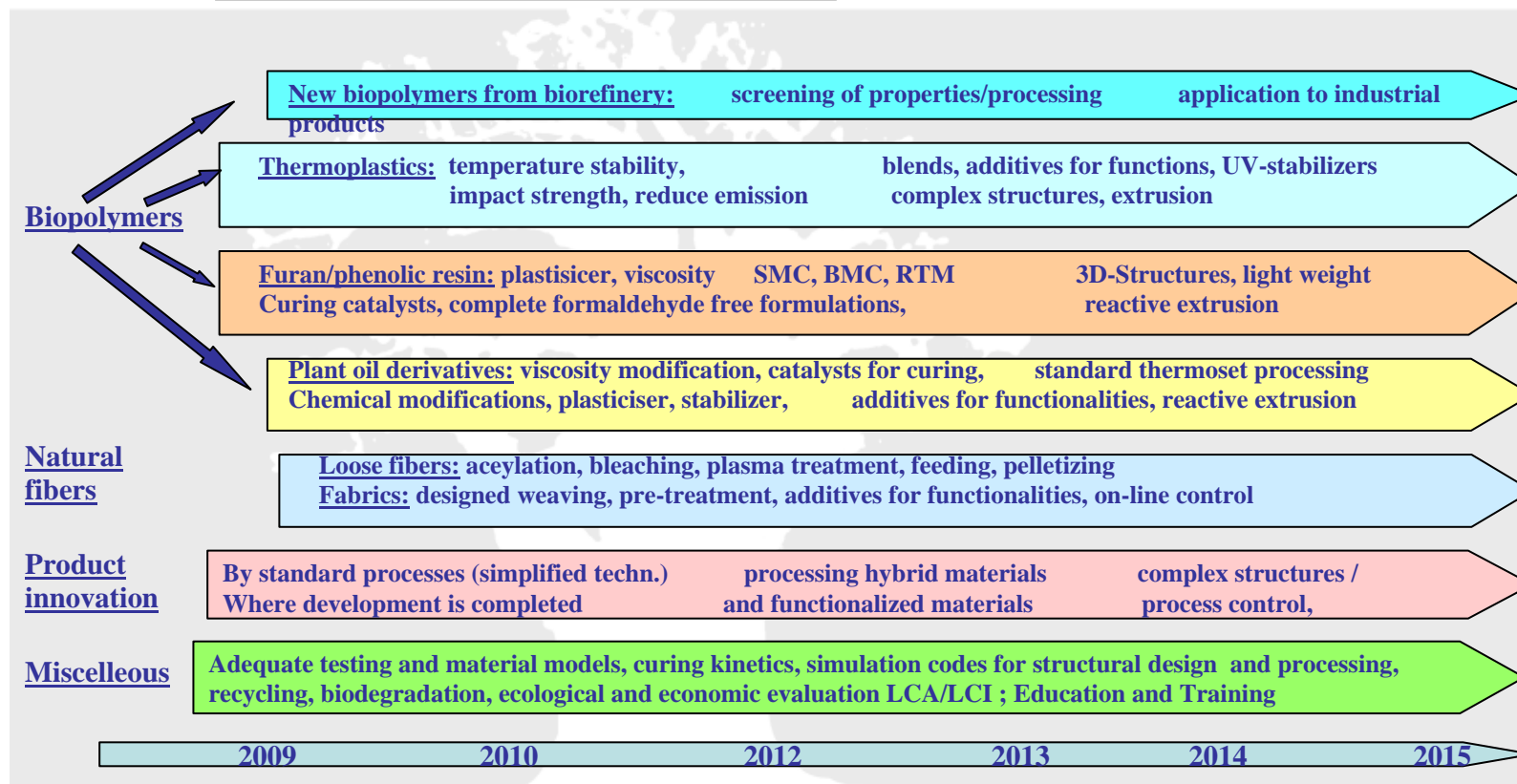
- Investigate more detailed material models for description of the mechanical and thermal behavior of biocomposites,
 - Improve **simulation** of **structures**, **moulding** and **curing** and needed data sets from testing or modify existing simulation codes according to biocomposite properties
- Processing:
 - More complex products by co-extrusion, multi-component injection moulding, foaming, back injection moulding, blow moulding, etc.
 - Develop hybrid materials, e.g wood/biocomposite structures or ceramic/metal/biocomposites and integrate surface finishing
 - Single step processing from raw materials to semi-finished or finished products, tailored fiber placement
 - Cover industrial branches of mass consumer, automotive, electronics, construction, furniture etc.
 - Use special technical advantages like acoustics, fire and chemical resistance or dimensional stability of biocomposites for design of innovative products,
 - Show benefits and drawbacks of materials including the eco-friendliness by a comparative Life Cycle Analysis
 - **Education/training:** Packages for education, training and practical workshops have to be update to address students, engineers, staff and material designers

In addition, industrial use and market penetration has to be supported. Especially progress-oriented SMEs should be given access to the resources of research institutes and receive their full support. These SMEs drive the product innovation using new approaches to exploit the obvious technical and economic advantages. However, R&D institutions are needed for support in overcoming the obstacles.

Figure 30 represents a roadmap for future needs of R&D to further support materials from renewable resources. A near term success requires parallel activities on the components of materials, the processes and products. In addition, funding programs should also support the introduction of completed developments to the market, as material innovation has to compete with the strongly subsidized energetic use of biomass.



Figure 30: Roadmap for biocomposite development



7 Summary

Biocomp materials use components completely or predominantly of biomass constituents together with natural fibers, partially from existing extraction processes like lignin and furans. Considering all investigated polymer matrices polylactide, starch, lignin, furan and crops oil based resins, the Biocomp composites could be processed using standard methods of plastic mass production. In addition, advanced processes like LFT-D of composite industries work also for Biocomp materials. This advantage enables a short or medium term commercialization. A substantial progress of the material development could be achieved towards properties of competing synthetic plastic composites and demonstrated by products manufactured under industrial condition. Extensive testing proved that the properties could be comparable to normally used synthetic polymer composites e.g. the mechanical properties. Unique materials in the world evolved from the project like the lignin and furan resin matrix composites.

A knowledge based approach based on modelling of material properties enabled structural and processing simulations. The measured material data available from the project provided an unusual broad basis for theoretical understanding and description of the behaviour of biocomposites. Structural design, processing and tooling could therefore use the industrially applied procedures for composites to moulds and part manufacturing. Consequently applied control like Near Infrared Spectroscopy and selection of raw materials could clearly refute the current pre-judices of highly scattering properties of biomass based components.

An LCI/LCA proved Biocomp raw materials, processes and products to offer sustainability when converting biomass to industrial composites. The impact occurs already within the agricultural and pre-processing of the various composite components. Being comparable in processing to standard composites a tendency to less energy usage for the biocomposites is expected. A continued improvement of processes would extend sustainability substantially, when rigorously supporting cleaner and more effective technologies.

Annex

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AbbreviationsList

ABS - AcrylnitrileButadienStyrene
BMC - Bulk Molding Compounding,
CRT, RCF - Cellulose Regenerated Fiber
DSC – Differential Scanning Calorimetry
E- modulus - Young’s modulus
EP - Epoxy resin
FR - Flame Retardant
GF - Glass Fiber
HDF – High Density Fiber board
HDT – Heat Deflection Temperature
HI-PS - High Impact PolyStyrene
IM - Impact Modifier
LFT-D-ILC - Long Fiber Reinforced Thermoplastics by a “Direct Process” with “In-line Compounding of matrix resins”
MDF – Medium Density Fiber board
MCR - Multivariate Curve Resolution
NIRS - Near Infrared Spectroscopy
NR - Natural Rubber
OSB - Oriented Strand Board
PA-11 - PolyAmide 11
PC - principal components
PCA - Principal Component Analysis
PLA - PolyLactic Acid, PolyLActide
PLRS - Partial Least Square Regression
PCL - PolyCaproLactone
PHB - Poly-3-HydroxyButyrate
PHBV - Poly(3-HydroxyButyrate co-3-hydroxyValerate)
PP - PolyPropylene
prepreg – pre-impregnated fabrics
RCF = Cellulose Regenerated Fiber
RMSEP - Prediction error
RH – Relative Humidity
Rpm - rounds per minute
RTM - Resin Transfer Moulding
TG - Thermo Gravimetry
TriAc - TriAcetine
TEC - TriEthyl Citrate
SMC - Sheet Molding Compounding,
Vf - fiber Volume fraction