PROJECT FINAL REPORT

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[1] Usually the contact person of the coordinator as specified in Art. 8.1. of the Grant Agreement .

[2] The home page of the website should contain the generic European flag and the FP7 logo which are available in electronic format at the Europa website (logo of the European flag: http://europa.eu/abc/symbols/emblem/index_en.htm logo of the 7th FP: http://ec.europa.eu/research/fp7/index_en.cfm?pg=logos). The area of activity of the project should also be mentioned.

1. Final publishable summary report

1.1 Executive summary

MINANO project was cooperation between five partners from Mexico, four from Europe and one from Brazil. The purpose was to create mass production capability of $Mg(OH)_2$ (MDH), ZnO and Ag nanoparticles in Mexico and to utilize them in Europe in plastic and wood-plastic composites aiming for commercial applications with improved performance in areas of flame retardation, UV-protection and antimicrobial and antifungal properties. Additionally the sustainability and safety of the production, further processing and use of nanoparticles was investigated.

Polypropylene (PP) was used for the plastic nanocomposites and polyvinylchloride (PVC) for wood-plastic nanocomposites (WPC). Additionally foamed polystyrene (PS) was used as a matrix in heat insulation elements for buildings.

The flame retardancy of polypropylene and polyvinylchloride-wood composites was improved by adding MDH as a mixture of micro and nano-sized powder. Polypropylene is highly flammable and requires about 65% of MDH in order to become classified as flame retardant according to UL94 V0 standard. By replacing 2-10% of the micron sized MDH with nano-size the smoke production and peak value of heat release rate were decreased. In wood-plastic composites the PVC was flame retardant itself, but the wood component was not. The use of MDH decreased the smoke production and heat release rate, but the benefit of using nano-MDH was not clear in this case.

Polypropylene and polystyrene are one of the most common plastics materials, but in general it has poor durability against UV and thus needs to be mixed with UV-protecting additives for outdoor use. In MINANO the UV protection of PP was improved by using nano-ZnO particles coated with aminosilane in 1% concentration, which in PP gave similar UV protection as commercial organic UV-protecting product Tinuvin 326 in 0.3% concentrations, which was used as reference. Nano-ZnO did not have the same problems as the organic material related to yellowing and micration to the surface. The UV stability of PS foam, heat insulation elements for buildings, was also improved by adding a mixture of nano-ZnO and Ag to the PS foam. The nano-Ag is known to perform as an antimicrobial additive and it was mixed with nano-ZnO in order to reduce the price and to provide simultaneously both UV-protection, antimicrobial and antifungal properties.

Wood plastic composite made of PVC and wood proved to be challenging due to their tendency to degrade over time by environmental effects like moisture and UV. These effects were mitigated by better encapsulation of the wood particles into the PVC plastic, by replacing part of the wood by MDH and by adding ZnO to absorb the UV radiation.

There are numerous possible commercial applications where the developed technologies could be used effectively. UV-protected PP is needed e.g. in a garden chairs, flame retardant PP can be used in electrical boxes and antimicrobial properties are required in air conditioning machinery. Wood-plastic composites are used e.g. in outdoor decking, railing, fencing and siding.

1.2 Summary description of project context and objectives

There are high expectations in the markets related to nanomaterials in various matrix material composites. Successful adaptation of nanotechnology in the end-products requires an access to the nanofiller technology and to the raw materials. The MINANO-project brings together partners representing end-user's product know-how, formulation and processing technology and most importantly secures a reliable source of nano raw materials. Although there has been tremendous development in the area of nanomaterials with improved functionality, there exists a need to develop an efficient, continuous method of large-scale, low-cost synthesis of such materials. To answer to this need the following steps are suggested:

1) Integrate the synthesis of the high-quality nanoparticles directly on the continuous mass-production process already in the mining industry,

2) Ensure controlled dispersion to the matrix material in large scale by cooperation between nanoparticle producer, processing and formulation providers and end-product manufacturers,

3) Assure sustainable and safe production and use of the functional nano-modified material by state-of-the-art life-cycle assessment.

Based on the mass production process and cooperative value chain we concentrated on three major functionalities: Flame retardancy, UV protection and antimicrobial properties. These properties were achieved by functionalized $Mg(OH)_2$, ZnO and Ag nanoparticles. Societal and industrial impacts of these properties are extensive and there is a strong request of these functionalities especially for plastic, but also for wood-plastic composite based matrix materials. The use of nano-sized functional inorganic filler materials enables better stability, recyclability, higher mechanical strength after ageing and potential multifunctional features to the end-product. The combination of new nano-functionalities gives far reaching possibilities for new types of functional plastics, and completely new possibilities to wood-plastic composites as well. This moves both the mining industry and end-product companies towards high-tech in the long run.

The early adapters of nanotechnology are able to look up the most favourable sources of nanofillers by working closely with suppliers. This could translate into a secure supply of key raw materials, or favoured pricing. While some end-material producers are trying to create nanocomposites through completely home grown efforts, the most successful ones are those with close access to the nanofiller technology companies. In MINANO-project Servicios Administrativos Peñoles SA (SAPSA) designed tailor made nanomaterials already in the early synthesis steps, which enabled more suitable nano-raw-materials for the end-product producers like So.F.teR Spa. (SOFTER), Sovere Spa. (SOVERE), Owens Corning Mexico SA (OWENS) and Owens Corning Fiberglass SA (OWFIB).

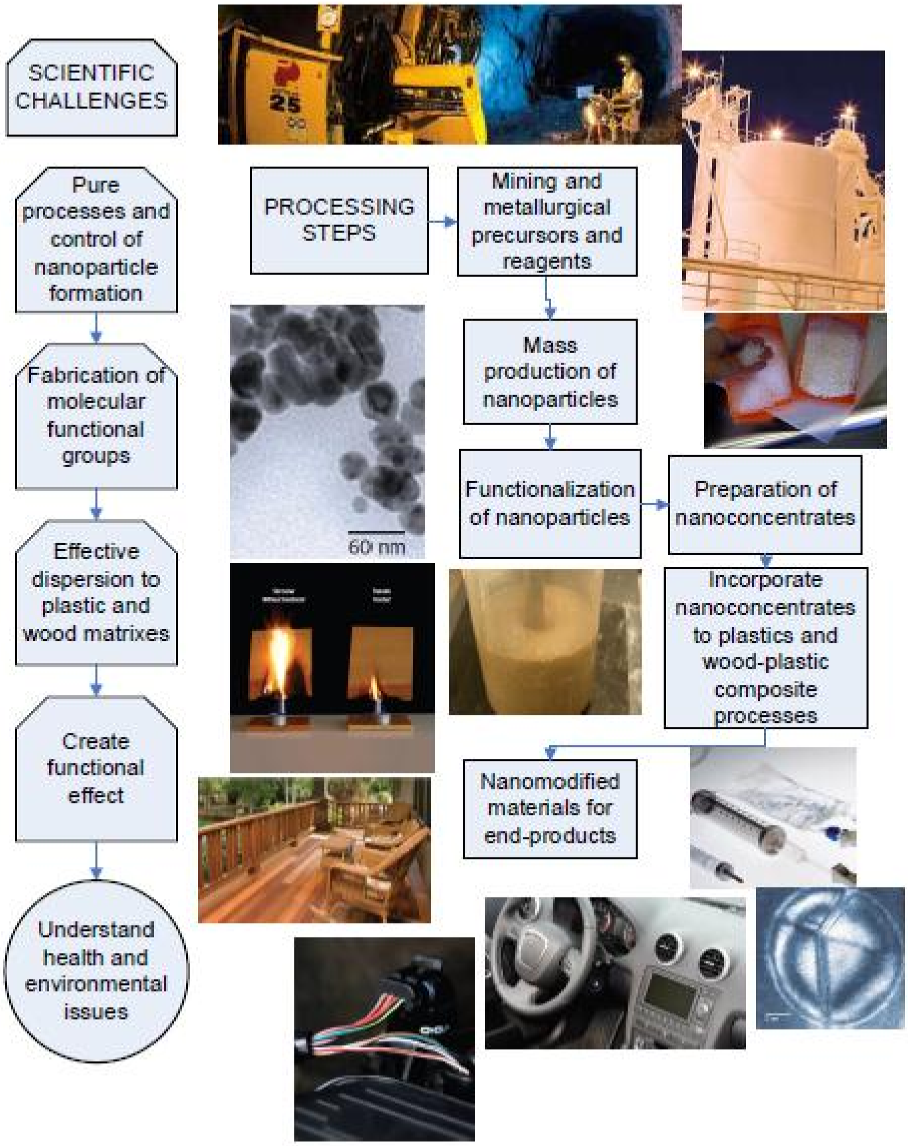

Figure 1. *The overall concept of MINANO-project.*

Access to nanocomposite formulation and process technology is absolutely critical to any successful participation in the industry. Compatibilisation between the nano filler and the base polymer is another critical success factor that must be highlighted. Successful nano-composites were developed by MINANO end-material producers SOFTER, SOVERE, OWENS and OWFIB that properly characterized the individual raw materials, understood the level of compatibility required between the nano and the matrix material, and produced a consistent nano-composite repeatedly. In general most companies are still at an early stage in their development of nano-modified products. This represents an opportunity for new entrants into the market as only a few suppliers have established strong brand identification or customer loyalty.

Technological aims:
- Mass production capability >5000 tons/year for $Mg(OH)_2$ and ZnO and >10 tons/year for Ag nanoparticles.
- Cost effective method to functionalize the nanoparticles: Use mining and metallurgical precursors including evaporite minerals (salt mines) to produce nanoparticles and to control their characteristics and properties
- Develop demonstrative samples that indicate the potential for upgrading the flame retardancy class of the end product by at least one with addition of <7%(mass) of nanoparticles in selected plastic and wood-plastic composite matrices.
- Achieve antimicrobial protection against two most typical fungi or bacteria in plastics, wood-plastic composite matrixes by using less than 0.1%(mass) of Ag and/or 0.1%(mass) ZnO.

Scientific aims:
- Create theoretical understanding for developing ZnO nanoparticles that improve UV resistance and demonstrate their economically viable performance especially in plastic matrixes such as polypropylene.
- Highly novel multifunctional (flame retardant, UV-protection and antimicrobial) properties in plastic and wood-plastic composite matrixes by addition of nanoparticle combinations ($Mg(OH)_2$, ZnO and Ag).
- Share of knowledge in plastic nanocompounds, wood-plastic nanocomposite products and LCA know-how.
- Environmental aspects: Reduce use of halogens in flame retardants. Improve recyclability for specific applications of plastic products by using sustainable inorganic functionalization by nanoparticles.

Societal aims:
- create long term research cooperation between EU and Mexico by:
    - o arranging researcher exchange between VTT and CIQA related to polymer nanotechnology
    - o arranging researcher exchange between DTU and CIMAV related to life cycle assessment

Overall strategy of the work plan:

The work plan was divided into 9 Work Packages. In WP1 “Production of nanoparticles” the nanoparticles were synthesized from mined raw materials in industrial mass-production scale. The high-quality and economically competitive output of the process was optimised by utilizing the reagents and precursors that were already used and available in the running mining processes. The work was done mainly by partner SAPSA and they were assisted by UASLP in characterization.

In WP2 “Functionalization of nanoparticles” the nanoparticles were functionalized for the selected flame retardant, UV-protection and antimicrobial functionalities so that they would be readily suitable for existing production methods used for the matrix material processing. The nanoparticles were dispersed e.g. in liquid suspensions or in plastic masterbatches. This minimized the amount of new investments needed in the end-product manufacturing when equipment optimized for current production was used without or with very little modifications. The functionalization work was done by SAPSA in cooperation with CIQA and CIMAV.

In WP3 “Nano-modified polymer-based materials” the laboratory work was done to ensure that the functionalized nanoparticles from WP2 could be well dispersed to the selected polymer matrixes. Laboratory and pilot-line scale processing equipment were used for processing the plastic nanocompounds and the materials were thoroughly characterized. Processing aid materials were added and the plastics processing parameters are optimised. Test samples were produced to help assessing the end-product functionalities. The work was done by partners CIQA, VTT, CIMAV, SOFTER and OWENS.

In WP4 “Nano-modified wood-plastic composite materials” the functionalised nanoparticles from WP2 were integrated to the wood-based (fibre, powder or chip) and/or plastic material matrix. The most suitable incorporation methods were developed and the effect of the nanoparticles on the overall performance of the composite structures investigated along with the new functionalities. The work was done by partners CIMAV, SOVERE and VTT.

In WP5 “Nano-modified material end-products” wood- and plastic-based end-product materials were produced by methods used in industry. The results from WP3 and 4 were used when taking the nano-modified materials to the industrial processing environment. The end-results were analysed by the methods that were typically used for the end-product evaluation depending on the customer requirements for each product and functionality. The end-product properties of the nano-modified compounds were compared with the state-of-the-art materials that were commercially available. The work was done by the industrial end-material producers SOFTER, SOVERE, OWENS and OWFIB.

In WP6 “Sustainability and safety” aimed to ensure environmental sustainability and the safety of the technology developments and was to increase information related to the life cycle environmental implications of nanomaterials mining, modification, use and disposal. This WP aimed to make assessment of conventional technologies, and to compare the developed technologies with the conventional technologies. The methodology used for LCAs conformed to the ISO 14040 and ISO 14044 and the International Reference Life Cycle Data System (ILCD) Handbook from the European Commission. The ILCD encompass a technical guidance document for impact assessment which was followed. The potential environmental and health risks of nanoparticles was of high concern. It was therefore also the intention to include more specific assessments of the potentials toxicological and ecotoxicological risks of nano-materials based on literature. The responsible partner in this work package was DTU and their cooperated with CIMAV.

WP7 “Dissemination and exploitation” prepare the methods and plans for publishing and protecting the results and exploiting them for industrial use. WP8 “Management” took care of the overall coordination and management of the project.

1.3 Main S&T results

1.3.1 Production of nanoparticles

The mass production capability of nanoparticles from inexpensive raw materials as a side stream in mining industry is a very promising prospect. The main issues in the nanoparticle production are the purity, shape, size and size-distribution of the nanoparticles. The processes to achieve the desired quality are explained here.

Nanoparticle Mass-Processing Parameters
During the early stages of the task development, analytical reagents were used in order to establish the synthesis protocol.

- For the synthesis of magnesium hydroxide nanoparticles, the selected precursors were: magnesium sulphate and magnesium chloride.
- For the silver nanoparticle's synthesis, the selected precursor was: silver nitrate.
- For the synthesis of zinc oxide nanoparticles, the selected precursors were zinc sulphate and zinc chloride.

Using these reagents, the critical parameters affecting the shape, size and size distribution of the nanoparticles were defined, without considering any impurities in the reactants. Trials included varying the precursor and reagents concentrations, and also excess alkali is varied. Other variables that affect the particle size are the stirring speed, retention time and temperature.

Once the synthesis protocol was established for each nanoparticle, the correspondent mining precursors were identified and characterized, as presented in the previous section, in order to identify its main impurities. The selection of the precursors was based on finding those currents that have the best characteristics, such as ions concentration, availability, accessibility, consistency in the concentration of components and impurities were relatively easy to remove.

The analytical reagents were substituted by the selected mining precursors in the synthesis protocol without any further purification. Only concentration adjustments were done when necessary. As a result, alterations in the produced nanoparticles were identified and related to the impurities in the mining precursors.

The most critical parameters or variables affecting the particle morphology, particle size and particle size distribution of the nanoparticles were defined as process conditions for each nanoparticle synthesis protocol. These parameters are:

- Reagents Concentrations (Supersaturation)
- Stirring Speed
- Retention Time
- Temperature
- Flow Rates

For each particle, the mining precursors were evaluated in order to identify its impurities and its effects on purity, particle size, particle size distribution and morphology of the final nano product.

- For the $Mg(OH)_2$ particles, calcium ions are the main impurity, affecting the particle size and shape.

- For the ZnO particles, magnesium ions and sulphates affect the purity, size and shape of the particles.
- For Ag particles, cooper ions affect the purity and size of the particles.

Control protocols for mass-production of nanoparticles

During the early stages of the task development, analytical reagents were used in order to establish the synthesis protocol. Once the synthesis protocol was established for each nanoparticle, the correspondent mining precursors were identified and characterized, as presented in the previous section, in order to identify its main impurities. The selection of the precursors was based on finding those currents that have the best characteristics, such as ions concentration, availability, accessibility, consistency in the concentration of components and impurities were relatively easy to remove.

The analytical reagents were substituted by the selected mining precursors in the synthesis protocol without any further purification. As a result, alterations in the produced nanoparticles were identified and related to the impurities in the mining precursors. Later on, purification methods were developed for each mining precursor according to a particular impurity mainly affecting the nanoparticle synthesis. Once purification of the raw materials was achieved, the nanoparticle synthesis protocol was adjusted when necessary. For each particle, the mining precursors were evaluated in order to identify its impurities and its effects on purity, particle size, particle size distribution and morphology of the final nano product. Purification of mining raw materials was done when necessary for each process.

For the $Mg(OH)_2$ particles, calcium ions are the main impurity, affecting the particle size and shape. For the ZnO particles, magnesium ions and sulphates affect the purity, size and shape of the particles. For Ag particles, cooper ions affect the purity and size of the particles. $Mg(OH)_2$ nanoparticles have been successfully synthesized from Epsom Salt, with a minimum of calcium and insoluble matter content. Ag nanoparticles have been successfully synthesized with both identified mining precursors. AgNO3 solution from Peñoles Refinery had to be purified in order to obtain the expected results. ZnO nanoparticles were synthesized with $ZnCl_2$ which is produced via dissolution of Zn dust or ZnO.

Stabilization of nanoparticles

The stabilization of the $Mg(OH)_2$ nanoparticles is made after the synthesis step, starting from the product slurry from the synthesis. The wet cake is dispersed with short chain fatty acids and dispersant, then taken through a drying process to remove water. Granulated powder is obtained which can be integrated into the polymer at high loads. Both the paste and the granulated powder are stable for up to six months without the nanoparticles change their size and / or shape.

The stabilization of the ZnO nanoparticles is made after the synthesis step. During the synthesis, no extra additive is used for particle stabilization. Starting from the product slurry from the synthesis and can follow two paths: used as it is or with a surface treatment. The selection of the path depends on the polymer type used in the masterbatch. The paste is mixed with virgin polymer in a high intensity mixer, which by effect of the high shear is heated and melted, and evaporates the water contained in the paste. The stabilization of the Ag nanoparticles is made after the synthesis step. During the synthesis, no extra additive is used for particle stabilization, since the reducer acts as a stabilizing agent. Starting from the product slurry from the synthesis the paste is mixed with virgin polymer in a high intensity mixer, which by effect of the high shear is heated and melted, and evaporates the water contained in the paste.

We conclude that:

- Controlling the content of Ca^{2+} in the precursors for the synthesis and adding some short chain fatty acids during the drying can be achieved $Mg(OH)_2$ nanoparticles stable and easy to disperse in the concentrates.
- Controlling the content of Mn^{2+} in the precursors for the synthesis can be achieved ZnO nanoparticles stable and easy to disperse in the concentrates.
- Controlling the pH value during the synthesis can be achieved Ag° nanoparticles stable and easy to disperse in the concentrates.

1.3.2 Functionalization of nanoparticles

The functionalization of the nanoparticles is created by an active layer that is introduced on the nanoparticle as a coating. It is called functionalization, because it will transfer the functional effect of the nanoparticle to the rest of the material composite. The role of the functional coating can be e.g. to help the nanoparticles to disperse to the plastic as single nanoparticles or to prevent direct contact of the nanoparticles with the matrix if the nanoparticles have intrinsic degrading effect on the plastic like nano-ZnO has on PP.

Bacteriostatic and fungistatic functionalization
Experimental Development
Concentrates were prepared using Polypropylene resins provided by Softer, with the integration of nanoparticles of silver and zinc oxide, to give the materials bacterostatic and fungistatic functionalities.

Silver nanoparticles were functionalized during the synthesis. The reducer acted as a stabilizing and functionalizing agent. Zinc Oxide nanoparticles were functionalized after synthesis with special surface treatments of silanes to avoid photo-catalytic effect on the application. Several functionalization approaches for coating nano-ZnO particles were evaluated like silane and silicon additives specifically tailored for ZnO. The silane coated was the best combination which gave excellent mechanical properties after UV aging.

The antibacterial additive BacFungi (BF) was introduced into a sample of SOFTER's typical compound called "Policor". Different amounts of BacFungi were tried in order to obtain the best concentration where the logarithmic reduction of grown (R4) were 2, this is, when the inhibition of microorganisms growth is almost 100%. Additionally, a sample with the SOFTER's additive (OM08) was evaluated to compare the performance to that of BacFungi Additive.

The antibacterial evaluation was performed by the UASLP and they evaluated the antimicrobial activity according to the Japanese standard JIS Z 2801: 2000, using the ATCC strain E.Coli 25922 for the initial samples without any UV exposure produced by SAPSA. The ATCC strains of E.Coli 25922 and S. Aureus 29213 were used for the samples with 120 hours of UV exposure. Antimicrobial evaluation of the strain *E. Coli* was done for the prepared samples, without any UV conditioning, i.e. time zero. For *E.Coli* bacteria the BacFungi additive shows good performance and compared to Softer's antimicrobial additive, better inhibition results are obtained with 0.3% and 1.0% of BacFungi in the formulation. With the middle concentration of 0.3% is possible to obtain inhibition of 99.2%.

Samples were later on exposed to UV radiation for 120 hours. After the UV exposure, samples were once more evaluated for antimicrobial activity. BacFungi shows good reduction on inhibition of *E.Coli* bacteria in all cases, while the sample with the lowest concentration of BacFungi remains with the same value.

Antimicrobial activity test of *S. Aureus* on samples that were exposed for 120 hours to UV radiation was also performed. The best results were obtained with BacFungi formulations with a concentration higher than 0.3%. It is important to note that the antimicrobial additive that SOFTER actually uses OM08 reaches 88.06% of inhibition while the sample BF10 with 0.3% of additive reaches 93.28% on inhibition; moreover with the highest concentration of BacFungi (1.0%) the best inhibition of 95.52% is obtained after 120 hours of UV exposure, which represents 3 months of exposure in an environment similar to Florida City.

Good inhibition results, above 90% are obtained for formulations containing 0.3% or above of BacFungi additive from Peñoles and in most cases it showed a better performance than the SOFTER's commercial antibacterial additive, even after samples were exposed to UV radiation.

UV functionalization

The ZnO nanoparticles' functionalization was carried out in order to avoid the photocatalytic phenomenon. The additive used as a quencher was a silane that covered the particle and prevented degradation reactions. The silane coating was the best combination, which gave good mechanical properties after UV aging, especially on elongation at break

Concentrates were prepared using polypropylene resins (Moplen HP400R, Moplen RP340N) with zinc oxide nanoparticles to improve performance on UV-Protection functionalities. Previous trials have shown that the best system comprises a composite with 1% of nano-ZnO in RP340N. Initially, the coated ZnO nanoparticles paste was incorporated to a mixer and mixed with EVA in order to obtain an EVA-ZnO master batch concentrate used for UV-protection with wood-plastic composites.

Additionally, a different route was evaluated. In this case wood flour samples were functionalized (pretreatment) by encapsulation of lignin fibers with a resin that is compatible with PVC and acts as a carrier for the nanoparticles. In this way, ZnO nanoparticles were integrated into the resin used for wood encapsulation which was compatible with PVC to get a better dispersion and homogenization of ZnO nanoparticles in wood-plastic composites.

RP340/ZnO samples were evaluated at ageing conditions according to ASTM D-4329 (Cycle A with condensation cycle, 180 hours) according to the information presented by CIQA. An Atlas UV test chamber was used for evaluation of UV exposure of WPC. The cycles used for wood-plastic composites were of 8 hours of light and 4 hours of condensation, using 340 nm lamps. Mechanical properties of the polymer were dependent of the ageing conditions. Moreover, the sample containing ZnO nanoparticles as additive showed the lowest decrease of this mechanical property with or without the condensation cycle. It is clear that ZnO nanoparticles had a better performance than Tinuvin 326 and Irganox B225.

For the wood-plastic composites, the problem of wettability in wood causes a discoloration. Pretreated Wood prepared by SAPSA, demonstrates to be a good option for avoiding the discoloration problem. Mechanical and physical properties were maintained.

Zinc Oxide nanoparticles were functionalized after synthesis with special surface treatments to avoid photo-catalytic effect on the application, achieving better performance on plastic nanocomposites than actual products in the market, i.e. Tinuvin. Encapsulated wood, together with ZnO nanoparticles was demonstrated as a good option to avoid the discoloration problem in WPC after UV exposure maintaining mechanical and physical properties.

Flame retardant functionalization

Functionalization methods used for MDH nanoparticles are similar to those previously used for micro MDH particles. In this case additives like stearic acid and silanes have been mainly used for functionalizing MDH nanoparticles, to improve dispersion and functionality of coupling the MDH mineral filler with the polymer matrix.

Concentrates were prepared using polypropylene resin RP340N with a blend of micro and nano particles of magnesium hydroxide (up to 65% weight) to improve performance on flame retardant functionalities. Samples were prepared by CIQA, and in order to improve dispersion of magnesium dihidroxide (MDH) particles, a polyethylene wax was used during processing as suggested by SAPSA. Also, EVA was used in the formulation so as to improve mechanical properties of the samples. More details are presented on reports of work package 3. A blend of micro and nano particles of $Mg(OH)_2$ was prepared, together with a slurry of this $Mg(OH)_2$ that was incorporated as a surface treatment of the wood flour. In the same way, another alternative was evaluated, adding the powder blend of dry micro and nano MDH directly to the wood-plastic formulation. This was defined as the best alternative to integrate the MDH to the compound. The usage of a PE wax during the processing of the samples, did not significantly affect the mechanical properties of the samples. While the content of MDH and the relation of micro and nano particles did have an effect on the performance of the samples. With an increase of the nanometric material, the ultimate tensile strength decreased. However, it is due to the increment of the EVA proportion in the formulation. The opposite happened with the impact strength, which was increased as the nanometric material and the EVA proportion in the formulation were increased as well. If we consider the results on the mechanical properties of the samples without MDH, we can see that this effect was caused by the presence of EVA in the formulation, and not on the presence of nanometric material. Furthermore the rate of reduction on the mechanical properties was roughly the same for all formulations.

From the studied systems, a deeper insight of the role of polymer matrix and its interaction with the morphology of MDH is still required. However, from this study it can be concluded that micro-sized MDH particles "HQ2060" in combination with RP340N/EVA in a composition of 40:60 is a good system to develop fire retardant materials with less content of micro-sized MDH particles. The system RP340N(PP)/EVA (40:60), MDH Micro50/Nano10 showed a lower decrease in the mechanical properties, especially in elongation at break, in comparison with virgin PP/EVA. When using MDH, especially HQ2060 MDH, it is possible to reduce the smoke production rate from 10-11 to less than 1 1/s.

For the wood-plastic composites with MDH, the best smoke suppression and HRR values were reached at 30% of MDH micro and nano of the total wood of the wood-plastic composite, which should not change too much from the original WPC product without mineral additives, as show in the figure below. Further information is presented on the reports of work package 4. Flame retardant applications were not the main commercial goal for SOVERE, while the discoloration and dimensional stability due to the moisture and environmental agent were the main challenge to solve for PVC-wood composites.

1.3.3 Nanomodified polymer-based materials

The WP3 was focused on the optimized ways to effectively disperse ZnO, $Mg(OH)_2$, and ZnO/Ag nanoparticles into polypropylene matrices, in order to obtain the functionalities of UV-resistance, flame retardancy and antimicrobial, respectively. In the early stages of the project, VTT and CIQA-SAPSA used different polymer matrices and processing conditions in the preparation of these polymer nanocompounds. Some challenges were presented concerning to the decrease of the negative impact that some nanoparticles had over the original mechanical properties of the polymers. However, new strategies were implemented in order to mitigate these effects. In this section a summary of the final functional properties (including dispersion) is presented for the polymer nanocompounds, obtained from the first attempts until the optimal conditions.

UV-Protection Properties
As first attempt, the preparation of polymer nanocompounds with UV-protection properties was characterized by the use of ZnO nanoparticles with different surface treatments. The ZnO nanoparticles were synthesized by SAPSA and coated with stearic acid and silanes moieties. Therefore, nanocomposites containing ZnO nanoparticles coated by stearic acid were used. However, the mechanical properties were negatively affected by UV degradation.

In this first approach, it was suggested than the surface modification and dispersion of the ZnO were not effective. Therefore, ZnO nanoparticles were submitted to double modification. In this procedure, acid stearic-functionalized ZnO nanoparticles were also coated by silane moities. The double modification of ZnO nanoparticles showed improvements in the mechanical properties of the nanocompounds in relation to acid stearic-functionalized ZnO nanoparticles. However, the elongation at break was equally affected.

The mechanical properties of the nanocompounds based on Moplen HP400R were more significantly affected by the UV-degradation than those for Moplen RP340N; therefore, this polymer matrix was excluded. The Moplen RP340N containing 1 wt% of ZnO nanoparticles was selected as the best formulation under the criterion “less amount and better properties”. Then, the mechanical properties of the nanocompounds based on Moplen RP340N (best formulation) were improved when the injection melt temperature was increased.

Based on lab-scale experiments, final processing conditions and formulations were established, and shared to SoF.TER, which developed these compounds at industrial-scale. Then, the final properties were measured by CIQA and VTT. The final formulation and properties are shown in the following tables:

Formulations-compositions:

Formulation	**Moplen RP340 (%)**	**Masterbatch RP340N/nano-ZnO at 10% (%)**	**Tinuvin 326 (%)**
(PP/nano-ZnO at 1%)	90	10	---
Reference (**a**) PP	100	---	---
Reference (**b**) PP-Tinuvin 0.3%	99.7	---	0.3

*All formulations contain Irganox B225 as antioxidant at 0.4 phr.

Final Properties:

Before UV degradation:

Formulation	Ultimate Tensile Strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
(PP/nano-ZnO at 1%)	26.90 ± 0.2	953.76 ± 66	704.0 ± 35
Reference (**a**) PP	27.20 ± 0.6	1098.82 ± 14.28	702.4 ± 61.02
Reference (**b**) PP-Tinuvin 0.3%	26.90 ± 0.4	965.84 ± 59.11	528.40 ± 225.08

After UV degradation:

Formulation	Ultimate Tensile Strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
(PP/nano-ZnO at 1%)	29.6 ± 0.3	1016.18 ± 106	313.2 ± 168
Reference (**a**) PP	30.0 ± 0.3	919.39 ± 54.88	266.80 ± 141.36
Reference (**b**) PP-Tinuvin 0.3%	29.8 ± 0.2	902.53 ± 108.23	67.2 ± 52.81

In general, the nanocomposites containing ZnO at 1 wt% showed a better performance under UV degradation conditions than the reference's samples. In this way, the planned objectives were successfully achieved.

Flame Retardancy

As first attempt to reach V-0 rating compounds, several compositions were made using the polymer matrices HP501L, HP400R, and RP340N. These compounds were prepared using micro-sized MDH particles coated with silane and stearic acid moieties at different grades (HQ2001, HQ2060, HQ Plus60). From these first attempts, the flame retardancy results of the compounds were promising, but unfortunately V-0 classification was not achieved. From these results, the RP340N polymer matrix and the micro-sized MDH particles coated by silane HQ2060 were selected in order to obtain suitable formulations.

Then, a set of experiments demonstrated that formulations derived from the compound of RP340N containing nano-sized MDH particles, coming from the masterbatch of EVA/nano-MDH, demonstrated to increase the elongation at break up to 8.7 %. Therefore, a new set of formulations containing EVA were developed. From these results, two formulations presented good mechanical and flame retardant properties with the less content of micro-sized MDH particles. The final formulations and properties are shown in the following tables:

Formulations-Compositions:

	COMPONENTS (%)			
Formulation	**Moplen RP340N (%)**	**Masterbatch: EVA containing nano-$Mg(OH)_2$ at 48% (%)**	**Masterbatch EVA containing nano-$Mg(OH)_2$ at 29% (%)**	**micro-$Mg(OH)_2$ (%)**
a (PP/EVA with a ratio 75:25, containing 50% Micro and 10% Nano)	30	20	-	50
b (PP/EVA with a ratio 40:60 containing 50% Micro and 10% Nano)	16	-	34	50

*All formulations contain Irganox B225 as antioxidant at 0.4 phr.

Final Properties:

	PROPERTIES				
Formulation	**Ultimate Tensile Strength (MPa)**	**Young's modulus (MPa)**	**Impact strength (J/m)**	**Elongation at break (%)**	**UL-94 rating**
a (PP/EVA with a ratio 75:25, containing 50% Micro and 10% Nano)	16.30 ± 0.1	528 ± 48	21.22 ± 3.51	7 ± 1	**V-0**
Reference (**a**) (PP/EVA with a ratio 75:25)	17.54 ± 0.2	639.34 ± 35	68.28 ± 2.56	591.10 ± 25	**No rating**
b (PP/EVA with a ratio 40:60 containing 50% Micro and 10% Nano)	8.16 ± 0.5 11.7 ± 0.2*	180.78 ± 15.6 446 ± 29*	166.47 ± 3.51 160.09± 8.21*	139.55 ± 27 71.3 ± 12*	**V-0** **V-0***
Reference (**b**) (PP/EVA with a ratio 40:60)	12.80 ± 0.2	350.21 ± 30	313.04 ± 42.27	588.71± 32	**No rating**

*Results obtained from the SOFTER´s samples prepared at industrial-scale.

The RP340/EVA polymer matrix in combination with micro-sized MDH particles "HQ2060" and nano-sized MDH particles was presented as a good system to develop fire retardant materials with suitable mechanical properties. The planned objectives were successfully achieved.

Antimicrobial properties

As mentioned previously on section 1.3.2 concentrates were prepared using Polypropylene resins provided by Softer, with the integration of nanoparticles of silver and zinc oxide, to give the materials bacterostatic and fungistatic functionalities.

The antibacterial additive BacFungi (BF) was introduced into a sample of SOFTER's typical compound called "Policor". Different amounts of BacFungi (Nano Ag / Nano ZnO) were tried in order to obtain the best concentration where the logarithmic reduction of grown (R4) were 2, this is, when the inhibition of microorganisms growth is almost 100%. Additionally, a sample with the SOFTER's additive was evaluated to compare the performance to that of BacFungi Additive.

Good inhibition results, above 90% are obtained for formulations containing 0.3% or above of BacFungi additive from Peñoles and in most cases it showed a better performance than the SOFTER's commercial antibacterial additive, even after samples were exposed to UV radiation. See section 1.3.2 for more information.

1.3.4 Nanomodified wood-plastic composite materials

The WP4 was focused on the optimization of ways to effectively disperse $Mg(OH)_2$ (MDH), ZnO and Ag nanoparticles to the wood plastic composite (WPC) matrix of in order to improve flame retardancy, UV resistance and antimicrobial properties. At the beginning of the project the goal for flame retardancy was to achieve UL94 V0 category for the WPC, but since PVC is already self-extinguishing material, the objective migrated to obtain a composite with improved properties of smoke suppression and heat release measured by cone calorimeter test ASTM E-1354.
Also, at the very early stage of project, the UV protection was thought to be achieved only by the use of ZnO nanoparticles, but by the middle term, the group faced a new challenge due to a the discoloration process of WPC caused by a combined effect of water absorption and UV light. However, along the second term of project, several methods and strategies were developed to overcome the issue. Antimicrobial properties were modified by a combination of Ag/ZnO nanoparticles dispersed in the matrix.

Flame retardancy
During the first half of the project, MDH was incorporated to the WPC by treating wood with MDH dispersion, and then, by using the treated wood, in the WPC formulation. another way to add the MDH was by direct incorporation of powder during PVC formulation. Incorporation by water dispersion didn´t show any effect on flame retardancy properties. Powder incorporation of MDH during PVC formulation had a better performance on cone calorimeter test since it showed diminution in smoke production and heat release. Due to these results, the use of direct powder was the selected method to incorporate MDH and its optimum concentration was studied. The compounding of these materials was done in a twin screw extruder, but a mixer chamber was also used without detriment of nanoparticle dispersion according with a study by electron microscopy. With the use of a mix chamber, also the flame retardancy properties were kept. Best formulation for flame retardancy contained 15 % w/w of MDH.

UV-protection
As mentioned before, at the first stages of project, the use and dispersion of ZnO nanoparticles was the main focus for the UV protection. The first conclusions were that it could be desirable to put the ZnO nanoparticles on the surface of WPC. By the project mid-term, the first trials were done using Genioplast lubricant with the aim of carry the ZnO nanoparticles to the compound surface during the extrusion process. Also, ZnO modified with free radical scavengers (FRS) were tested for photocatalysis activity inhibition and samples containing FRS modified ZnO were prepared. Nevertheless, a discoloration, showed by the samples during UV-Aging test under moisture conditions and according with previous experience from SOVERE, it was concluded that, a combined effect of moisture and UV light exposure, produces the discoloration in the WPC.

To overcome the water absorption, several strategies were taken by the WP4 group. One of them was the use of silane treated SiO_2 nanoparticles to make the composite more hydrophobic. Also, a skin containing PVC/ZnO nanoparticles was prepared to paste on the WPC matrix simulating a coextrussion process. Another strategy was the treatment to wood by several methods: Acetylation, encapsulation and thermal treatment. The use of additives including plastizicers was also tried. All the treatments had the aim to diminish the water absorption by wood and to protect the matrix and/or the wood with ZnO during the UV aging test.

The best way to avoid discoloration was the use of plasticizer additive in the formulation together with ZnO nanoparticles. Another method that showed good protection against discoloration is the encapsulation of wood. Such process consists of a pre-treatment given to the wood with a polymer dispersion that includes ZnO nanoparticles. After the treatment, the wood is surrounded by the polymer that has trapped ZnO nanoparticles. Both methods avoid the absorption of moisture and keep good mechanical properties. Based on the results mentioned above, the formulations recommended for scale up were that containing encapsulated wood and plasticizer additive.

Antimicrobial Functionality.

Antimicrobial property was the last studied functionality. The main goal was to achieve 90 % of bacteria/fungi growth inhibition. Silver nanoparticles were incorporated to the matrix. The incorporation method was to add Ag nanoparticles in the matrix of WPC using chamber mixer and twin screw extruder. During the second half of the project, it was stated that a good protection against bacteria and fungi could be the achieved by a combination of Ag/ZnO nanoparticles. The second method was a simulation of coextrussion process by the use of a thin skin prepared with PVC and Ag/ZnO nanoparticles mix. Finally, the last trial was the use of an Ag/ ZnO nanoparticles mix that was added to the whole matrix using a twin screw extruder.
Although there was an inhibition showed for some samples, the 90 % of inhibition was not achieved.

Next, a brief description of the main results obtained for the finals compositions (recommended for the scale up test) are presented and compared against reference materials.

Final formulations:

Final formulations recommended for scale up test and references without nanoparticles are described in the next table.

Sample	Composition
SC503515	**PVC:** 50 % w/w (formulation from SAPSA) **Encapsulated wood:** 35 % w/w (formulation from SAPSA includes 2.8 % of nano ZnO, it means:1 % ZnO in the whole matrix) **HQ2015:** 15 % w/w (**$Mg(OH)_2$** prepared by SAPSA)
SC503515BF	**SC503515:** 89 % w/w **EVA nanoconcentrate:** 11 % w/w (containing 4.5 % of ZnO/Ag, it means: 0.5 % of Ag/ZnO nanoparticles in the whole compound)
M1_917	**ThermoGran:** 89.29 % w/w (is a PVC-wood composite prepared with the standard PVC formulation of SOVERE containing 1:1 of PVC wood)

	Plasticizer: 5.36 % w/w **Nano ZnO**: 5.36 % w/w
Reference SOVERE	**WPC** prepared at SOVERE México**,** according with standard formulation from SOVERE México.
Reference M1_910	**PVC mixed with thermally treated wood 50/50 %**

Formulation called SC503515 is a composition that includes MDH and ZnO nanoparticles with the aim to test on one composite both functionalities: Flame retardance and UV protection. M1_917 involves only UV-protection functionality.

The results of flame retardancy properties of cone calorimeter test performed to the final composition is summarized in next table:

Sample	Time of ignition (s)	Total heat release (MJ/m^2)	Smoke Production (SA) (m^2/m^2)	Mass Loss (%)
SC503515	57.5	18.3	821	21.34
Reference SOVERE	46	45.1	2252	78.97

It is observed that heat release and smoke production diminish to less than a half of the original values. Based on these results, it could be said that the flame retardancy functionality was achieved.

The results for UV protection (measured by colorimetric value DE after 3, 7 and 14 days of UV light and moisture exposure), water absorption (measured as the weight increase after 120 hours of immersion), and flexural test are sumarized in the next table

Sample	Aging/discoloration			water absorption	Flexural test
	DE Value			*Weight gain (%)*	*Flex. Modulus (MPa)*
	3 days	7 days	14 days		
SC503515	15.5	21.82	33.61	1.41	4112.84
Reference SOVERE	30.76	35.82	37.8	9.18	N.M.
M1_917	2.83	7.96	13.62	3.39	6288
Reference M1_910	37.18	44.17	44.72	2.9	6055

The summary table shows that there was an improvement in UV protection, especially in sample M1_917 since the DE value is the very low compared with the references samples. SC503515 showed improvement in UV protection and in water absorption although the flexural modulus diminished. According with this results, the UV protection functionality was improved and the objective was achieved and the discoloration and water absorption issues were overcome.

Related to the antimicrobial functionality, the best result was achieved when Ag/ZnO nanoconcentrate in EVA was incorporated to the whole matrix (not only in the surface as skin) as the formulation SC503515BF showing 61 % of cytotoxicity against Staphylococcus aureus ATCC 29213 and 9 % against Pseudomonas aeruginosa ATCC 15442. The optimization of antimicrobial functionality did not achieve the 90 % of cytotoxicity planned at the beginning of the project.

1.3.5 Nanomodified material end-products

1.3.5.1 Polypropylene nanocomposites

MINANO consortium is committed to achieve anti-UV-protection, flame-retardancy and antimicrobial protection of plastics using modified nano-fillers (nanoparticles of zinc oxide, magnesium di-hydroxide and silver) instead of traditional additives. Currently these functionalities are achieved by use of micro-sized inorganic additives and of organic additives.

Primary goal in using nano-fillers in polypropylene matrixes is obtaining nano-composites competing in terms of industrial productivity, of performances and prices with standard plastics, with an additional eco-friendly added value.

In particular one aim of the project is to verify if moving to nanotechnology can consent to achieve the following remarkable advantages beyond current state of the art.

Replacing standard micro-sized inorganic additives with nano-sized inorganic powders may result in the following advantages:

- Lower mineral loading needed and hence reduced loss of mechanical performances
- Enhanced efficiency and effectiveness per quantity of additive added
- Lower haze/higher clarity/neutral colour (in transparent or coloured polymeric matrixes)
- Lower yellowing and discoloration effects

Replacing standard organic additives with nano-sized inorganic fillers may result in the following advantages:

- No loss of effectiveness in time
- Lower migration out of the material
- High temperature processability and higher thermal stability
- Reduced loss of effectiveness while recycling
- Neutral colour when compared with some organics
- Higher environmental friendliness (for Flame-Retarded and Anti-Microbial materials)
- No incineration and recycling problems (for Flame-Retarded materials)
- Lower acidity of combustion smoke (for Flame-Retarded materials)
- No use restriction according to EU normative.

In fact EU normative is restricting the use of some of current organic additives (for ex. halogenated FR agents and some biocides).

In MINANO project the production of polypropylene-based nano-compounds was performed starting from laboratory-scale machinery and then scaling-up the results and processes to semi-industrial machinery. Trials were carried out on pilot-scale machinery with the purpose of replicating experiments performed in the previous work, defining primary machinery settings. Another pursued goal was fine-tuning the machinery settings in consideration to industrial and productivity issues. Moreover attention was paid to defining safe operating conditions.

The subsequent semi-industrial scale production were aimed at validating findings gathered from small scale experiments and at defining industrial processing conditions.

On a preliminary approach upper-limit processing conditions were identified in order to improve productivity and preserve final properties. Moreover the best screw profile and machine set-up were identified in order to have a good dispersion and to avoid overheating due to friction.

Subsequently industrial scaling-up were accomplished with satisfying results, in fact suitable processing parameters and machinery configuration were defined and industrial nano-composite compounds were produced on a semi-industrial co-rotating twin-screw extruder.

In an industrial scaling-up perspective some favourable matters were verified, which are of primary importance in a prospect focused on productivity and exploitability, and are summarized hereinafter. Interesting results were observed, that can be exploitable at industrial and commercial level. It is important to highlight that this nanotechnology can be applied to existing manufacturing processes without modification to the equipment, in fact no investment concerning new equipment should be needed in order to be ready to enter the market with these new products. Nanoparticles, once embedded in a masterbatch, can be mixed in formulation and processed in the same way as traditional raw materials achieving a satisfying dispersion degree.

Moreover prominence should be given to the fact that the possible benefits stemming from inorganic nano-fillers can be transferred to standard commercial formulations, which at present contain organic additives. For these reasons it is possible to foresee that materials based on this new technology will not lead to a significant increase in production costs in terms of processing equipment.

A set of testing procedure including physical-mechanical characterization of the materials, SEM TEM and optical microscope analyses, UV-VIS and IR spectroscopic analyses, UV-aging and weathering tests, UL 94 test and antimicrobial test JIS Z 2801:2000 were performed on the produced industrial nano-composites in order to assess their final functional efficiency. In particular the UV-protection performance of the nano-composite based on nano-Zinc Oxide was evaluated by comparison with a benchmark material treated with a common organic UV-protector (Tinuvin 326 from BASF).

With regard to performance and functional results we can draw the following conclusions. In general the physical-mechanical and functional properties observed at lab scale for the nano-composites were not only preserved, but also improved in the industrial scaling-up stage. The combination of nano-ZnO and nano-Ag provided to PP matrix a satisfying and efficient antimicrobial action against Staphilococcus Aureus and Escherichia Coli even if it affects the final colour of the material, which is dark grey.

The anti-UV performance of the industrial nano-composite containing 1wt% nano-zinc-oxide was quite good even if it does not reach the performance of the reference material containing Tinuvin 326. In fact after UV-aging and weathering surface degradation and yellowing of the nano-composite specimens was observed with resulting worsening of mechanical performance.

The combination of 50% micro-MDH and 10% nano-MDH provided a satisfying self-extinguishing behaviour to the PP matrix. The industrial sample was rated satisfactorily with

regard to self-extinguishing standard method UL94. In particular it achieved the best ranking (V0). The good reproducibility of data for different specimens was a proof of the achievement of good dispersion of the filler inside the material.
The production of this high MDH-filled material requires some additional care in comparison to standard FlameRetarded materials. However, health and environmental drawbacks of standard organic flame-retardant agents must be considered in the overall evaluation.

The technical work shows encouraging results and underlines that there is still room for further technical improvements. Some matters, which might be dealt with in further studies concern colour darkening and colour issue of material containing nano-silver particles and a comparison of the thermal stability of zincoxide nano-particles versus traditional organic additives.

1.3.5.2 PVC-wood composites

WPC-products are new types of composite materials that have been booming in recent years. The most widespread use of WPCs is in outdoor applications (Fig. 2), like deck floors, but sometimes WPCs are also used for railings, fences, landscaping timbers, cladding and siding, park benches, molding and trim, window and door frames, and indoor furniture. WPCs are composite materials made of wood fiber/wood flour mixed to the thermoplastic polymer.

Figure 2. *Some examples of WPC for outdoor applications*

WPCs are more environmentally friendly than simple plastics and requires less maintenance than simple wood: additives such as colorants, coupling agents, UV stabilizers, blowing agents, foaming agents, and lubricants help tailor the end product to the target area of application. Anyway, WPCs are still new materials relative to the long history of natural lumber as a building material; this means that they have lots of positive properties, but are still affected by some negative issues. The wood particles are susceptible to fungal attack, though not as much so as solid wood, and the material is still vulnerable to UV degradation and discoloration; it is possible that the strength and stiffness may be reduced by moisture absorption and freeze-thaw cycling, though testing is still being conducted in this area. Some WPC formulations are also sensitive to staining from a variety of agents.

So far, the biggest issue of PVC-based WPCs for outdoor application is the discoloration overtime (Fig. 3)

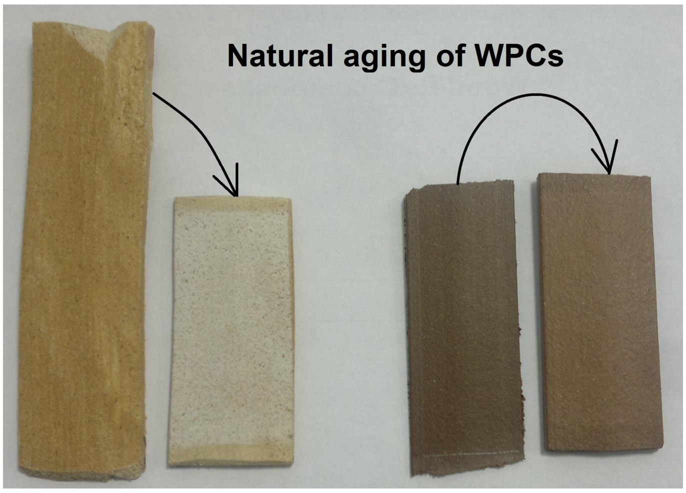

Figure 3. *Typical examples of WPC discoloration*

Over the years zinc oxide (ZnO) nanoparticles have attracted much interest, because they possess various remarkable physical and chemical properties, like good transparency and UV absorption properties [1]. The incorporation of nano-ZnO as UV-protecting agent into a polymer matrix have attracted particular interest in academic and industrial research [2]. In this work we have tested the colour-fading resistance properties of innovative PVC-based WPCs, filled in many ways with different kind of ZnO and functionalized ZnO nanoparticles. The effectiveness of ZnO nanoparticles for protection of WPCs against discoloration were studied under controlled UV ageing “dry / wet” conditions (“dry / wet” conditions were used to obtain a more realistic aging of the materials).

The first results showed that the UV-induced photodegradation effects could be only slightly reduced as compared with neat polymer. We discovered that the potential anti-UV activity of nano-ZnO was masked by the strong discoloration of the wood matrix, which is always induced by moisture. Due to this fact we understood that a protection of the wood particles against moisture seems to be mandatory, so we started using alternative approaches in order to do that.

In collaboration with all the involved partners, new kind of hydrophobic additives were tested into the WPCs, in association with nano-ZnO, trying to obtain a synergistic effect by increasing hydro-repellency and anti-UV properties. The protection of the wood particles against moisture seemed to be the right way to go through, so new functionalized nano-ZnO additives were developed and the resistance of the so produced WPCs was tested verifying an improvement of the resistance against moisture- and UV-induced discoloration. Also an improvement of the dimensional stability of WPCs under wet conditions was achieved.

A secondary approach was to use a pretreated wood flour called Thermowood® (ThermoWood® is a registered trademark owned by International ThermoWood Association), which should be more resistant to the atmospheric agents. Thanks to their improved durability against decay, the products made with this kind of wood are well suited to applications involving demanding weather conditions. Sovere made a preliminary scale-up of PVC-WPC compounding using this new raw material, in comparison with a standard wood flour, in order to setting up the right industrial process conditions. This work lead us to generate very good sample of both materials, obtaining WPC granules and beautiful extruded sample profiles.
The preliminary test on these new materials seems to be promising.

So far, the obtained results seem to indicate that the strategy chosen by the R&D partnership is the right way to go through and the nano-ZnO, when associated with the right hydro-repellent functionalities and the best wood flours, can increase the resistance of WPCs against natural atmospheric agents. Also, we can say that semi-industrial scaling up can be done without plant modifications. Nano-materials can be used mixing them to wood flour and PVC as traditional raw materials.

REFERENCES

1. Moezzi, A., A.M. McDonagh, and M.B. Cortie, Zinc oxide particles: Synthesis, properties and applications. Chemical Engineering Journal, 2012. 185-186: p. 1-22.
2. Ammala, A., et al., Degradation studies of polyolefins incorporating transparent nanoparticulate zinc oxide UV stabilizers. Journal of Nanoparticle Research, 2002. 4: p. 167–174.

1.3.5.3 Polystyrene foam composites

The Foamed polystyrene boards are typically used as insulation for constructions in residential as well as commercial buildings due to their low thermal conductivity and excellent moisture resistance. Since foamed polystyrene boards are a closed-cell product there is no water infiltration that can cause further problems within the insulation board itself; however, the presence of moisture in an enclosed space can cause fungal and bacterial problems if the insulation product installation was not properly carried out. It is in this respect that antifungal and antibacterial properties inherently in the product may give a distinct competitive position and can enable the use of this type of products in current and new applications.
Additionally, one of the weaknesses of foamed polystyrene is the degradation that it exhibits when exposed to UV light. When installed, the product is typically covered from UV radiation; however, operations such as transportation, storage and handling may expose the product to it and affect its performance. If UV degradation resistance can be achieved without major manufacturing process modification, simple operations such as transportation and storage can be further simplified.

In the framework of MINANO project zinc-oxide and silver nanoparticles synthetized in a previous stage were mixed with polystyrene in order to produce expanded PS-based nano-composites for thermal insulation in buildings.
Production experiments were run at different process-scale in order to validate the industrial process.

In a preliminary approach, trials were carried out on a laboratory-scale extruder in order to define the more effective concentration of nano-ZnO (tested concentrations were 0.05, 0.15 and 0.30 wt%) and to evaluate the effect of nanoparticles on processing conditions and on physical properties. No substantial differences in physical properties such as density and average cell size were observed.

Some feasibility trials were carried out on a pilot-scale machinery with the purposes of

- determining the use of UV-protecting and fungistatic nanoadditives,

- determining safety operating and processing conditions for the use of nano-ZnO for UV-protection
- determining safety operating and processing conditions for the use of the bacfungi mix (nZnO/nAg in the ratio 9:1) for anti-microbial protection.

In these experiments the masterbatches containing the nanoparticles replaced the colorant in the formulation and the final nanoparticle concentration was 0.08wt%. Subsequently another set of trials was run in the pilot line extruder with the aim of determining the optimal concentration of UV-protector nano-ZnO. Nano-ZnO masterbatches were used, having a UV-protector concentration equal to 1.62, 3.25 and 5.42wt% and three materials were produced with a final concentration of nano-ZnO equal to 0.50, 0.30 and 0.15w%, respectively.

In a further stage a processing experiment on large scale was run on an industrial extruder with the aim of validating the results gathered in previous trials and determining the repeatability of the results already achieved. UV-protected boards were produced and the final nano-Zinc-oxide concentration that was tested was 0.50wt%. The nanoparticles were handled in the form of a Masterbatch having a UV-protector concentration equal to 5.42wt%. Also industrial processing conditions were defined in order to obtain a uniform structure and to achieve a standard and regular thickness for closed cells inside the produced foamed polystyrene boards. In particular the extruder pressure was monitored in order to reach stable processing conditions and a post-expansion H3 process was implemented.

Being the expanded polystyrene used for thermal insulation within a building structural component, a particular attention was paid to possible variation of physical properties during the production of nano-composites in order to find the right processing conditions and to obtain a uniform structure for closed cells inside the foamed board. In particular density, average cell-size and cell-orientation, compressive strength and thermal conductivity were evaluated for the specimens produced at different process-scale Variations from the reference material (free from nanoparticles) were not significant and fell within the statistical standard deviation of the experiments.

Also functional properties of the produced polystyrene-based nano-composites were tested. Results of a performed UV-resistance test seemed to show an important reduction in UV-induced discoloration.

The following conclusions can be drawn:

- UV-test performed on nano-composites containing zinc-oxide showed interesting results.
- Nanoparticles did not seem to affect the process in the % amount of use, in different process-scale experiments.
- No significant variations were observed in physical properties such as density, cell size and thermal conductivity of the expanded materials.

In conclusion the experiments proved successfully that it is feasible to use nanoparticles in the manufacturing process of polystyrene insulating foam board without any major impact in process variables. According to tests and measurements performed on samples, the experiments proved successfully the repeatability in the industrial scale process.

1.3.6 Sustainability and safety

In WP 6 the overall objective was to ensure environmental sustainability and safety of the developed technologies. The WP encompassed a number of tasks aiming to achieve this. An initial screening of the main causes of environmental impact as well as a safety assessment related to the nanomaterials in use aimed to optimise the eco-efficiency of the technological developments in the project a.o. through development of eco-efficiency indicators for production within each work package. A continuous update of the initial assessments aimed to contribute with decision support concerning environmental and safety issues during the entire project from research and development to the final products used by end users. The final outcome should aim to establish Life Cycle data sets for the developed technologies and perform life cycle assessment of these as well as document potential environmental improvement in relation to conventional technologies.

The initial life cycle screening published in D 6.1 aimed to identify the main causes of environmental impacts in the production chain foreseen in the project, see example in figure 4 . It was based on readily available data and assessed two polypropylene products containing either Ag or ZnO – respectively air-condition part and garden chair.

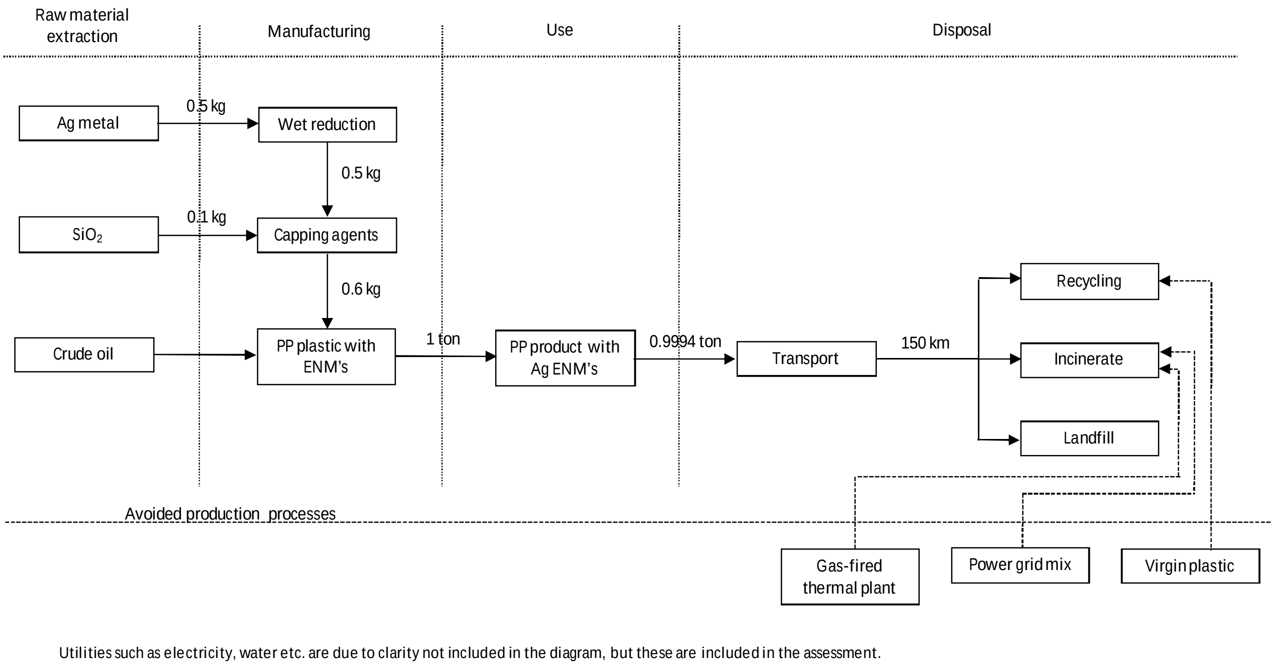

***Figure 4**: Production chain of a polypropylene product (part of an air conditioning system) with silver nanoparticles providing antimicrobial properties to the product.*

Additionally, the human and environmental safety of using the metal nanomaterials was assessed via a literature review of the three targeted ENPs (Engineered nano-particles) focusing mainly on how they behave in the environment (the fate) and what effects they can have on the organisms living there. The life cycle screening shows that the two example products differ with respect to which environmental impacts they cause and what cause the impacts. Where polypropylene production and silvernanoparticles production is the main causes of impacts for the air conditioning part (polypropylene and silver nanoparticles), the production of zinc oxide nanoparticle does not contribute a lot to the impacts of a garden chair (polypropylene and zinc oxide nanoparticle). Different scenarios for end-of-life show that for the air-condition part recycling has lowest overall environmental impacts, while incineration will cause less toxic impact. For the garden chair the screening gives incentive for incineration and secondly recycling (if disregarding climate change impacts). Energy recovery of waste through incineration is being favoured because the environmental impacts are saved due to substitution of heat and power that would otherwise be produced from mainly non-renewable sources. However, only polypropylene from the products is considered in the disposal scenarios, since knowledge on the potential impacts of nanoparticles in this stage were not available.

The fate of metal ENPs, including metal-oxides depend on the physico-chemical properties of the ENPs as well as on the which environmental compartments (water, soil and air) they are released to. In water the aggregation and dissolution of the ENPs are considered important, while in soil also the partitioning between solution and the solid phases plays an important role. The physico-chemical properties that seems to be most important for the fate and in the end effect of ENPs are: Size, particle number concentration, surface area, surface charge and solubility. These pathways and properties will be determining for the effect of ENPs on organisms if ENPs are released from the product. The important chain of release, fate, and exposure can be simulated with mathematical modelling to quantify the effects on organisms. However, the current knowledge is too limited to make precise models. Nonetheless, it can be concluded from the literature reviewed and toxicity tests performed that Ag ENMs (Engineered nano-materials) is more toxic than ZnO ENMs.

In order to qualify (and quantify as far as possible) how much of the nanoparticles in the plastic will potentially be released to the environment during use of the product four degradation tests were performed on polymeric nanocomposites with optimal formulation, specifically with excellent engineered nanomaterials (ENM) dispersion into polymeric matrix. Two tests simulated conditions for usage stage during materials life cycle, being mechanical fatigue induced by sharp thermal shock cycles and exposure to UV radiation combined with corrosive environment (salty fog chamber). Other two tests were carried out to assess final stage (grave stage) for materials life cycle, as disposal into sanitary landfill (acid hydrolysis degradation) and incineration (combustion into calorimetric cone). As expected polypropylene with very low quantities of ENM was resistant against hydrolytic degradation, thermal induced mechanical fatigue and exposure to severe weathering (foto-oxidative plus corrosive degradation). In the case for PP with major amounts of Fire Retardant ENM it had very low magnesium releases for acid hydrolysis and thermal shock. PVC-Wood compounded with Mg(OH)2 and ZnO ENMs showed that with optimal formulation the releases of metals of concern (Zn and Mg) were not statistically significant when subjected to acid hydrolytic degradation; while when it suffered combustion magnesium remained in ashes as MgO not being delivered to airborne particles flowing with combustion gases.

A more complete life cycle assessment (LCA) has been performed, where the potential environmental impacts of using plastic functionalised with nanoparticles (for antimicrobial, UV-protection, or flame retardancy) is compared to using plastic containing additives that are normally applied today. 5 products were considered; Polypropylene (PP) car air-condition part (enhanced antimicrobial properties), PP garden chair (improved UV-protection), PP small electrical box for households (improved flame-retardancy), PVC-wood outdoor flooring piece (improved UV-protection), Polystyrene (PS) indoor insulation sheet (improved UV-protection). It was not certain whether these products will be in actual production after the end of the project.

The data, used for performing the LCA on the proposed production technology of ENMs and polymers, was mainly collected from SAPSA during several rounds of data collection. The detailed LCA showed where in the product life cycle the highest environmental impacts occur. Production of nanomaterials has a relatively high environmental impact but the main contribution arise from the production of polymers used with ENMs (Ag, ZnO and Mg(OH)2). This is because the polymers used with Ag and ZnO ENMs make up approximately 99 % of the final polymer product. However, when producing adequately flame retarded polypropylene the final product contains ca. 60 % Mg(OH)2. This high content of (a mixture of micro-sized and nano-sized) Mg(OH)2 results in different environmental impact picture than for the Ag and ZnO ENM cases since the Mg(OH)2 is responsible for the main impacts.

The comparative evaluation, based on data collected within the consortium and on generic data from several LCA databases, showed that the polymers containing nanomaterials has a higher environmental impact than those containing the conventional additives. This was the case for all combinations of polymers and nanoparticles investigated (PP-Ag, PP-ZnO, PP-Mg(OH)2, PVC-wood – ZnO, PS-ZnO). As previously noted, the highest difference was seen for the PP-Mg(OH)2 due to the high content of micro and nano Mg(OH)2 (~60 %). This comparison was based on 1:1, where the functionality of the final products was assumed to be similar in terms of age spent in the use stage. This is a probable assumption since it is often not the durability/functionality but rather fashion that determines the lifetime of a product.
Nonetheless, due to the improved product functionality, provided by the use of nanomaterials additives, the final products could potentially be used for a longer time by the consumers. Within the project and in literature the potential improved functionalities of polymers with nanomaterials additives have been measured. These measured improvements of Ag-microbial reduction (air-conditioning part), ZnO-UV-absorption (garden chair), ZnO-UV-discoloration (outdoor flooring) and ZnO-UV-discoloration (outdoor storage of insulation sheets) were used as weighting factors, assuming a longer functional life time of the products containing nanomaterials. It was not possible to assume an improvement for the Mg(OH)2 used in small electrical box, as it is solely classified with the best (V-0) flame retardance properties within the grading. The potential benefit of using Mg(OH)2 (i.e. avoiding the use of halogenated flame retardants which are generally considered very harmful for humans and the environment) was investigated through assessing the potential carcinogenic and non-carcinogenic impacts of using DECABDE, which is a commonly known flame retardant although being widely substituted due its health and environmental impacts.

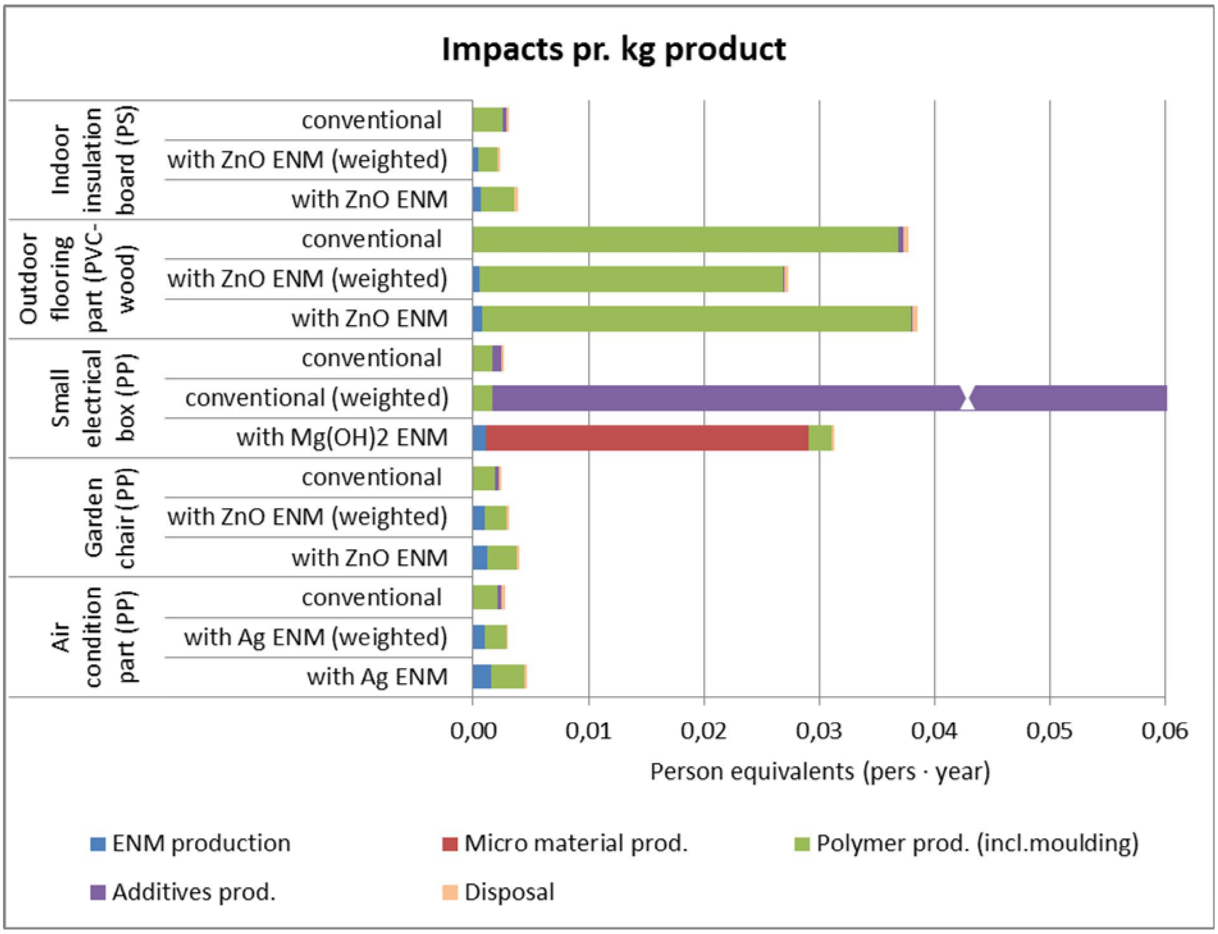

Figure 5. *Aggregated environmental impacts (default weighting factor of one) for different products, conventional approach compared with the use of ENMs in products to improve antimicrobial (Ag), UV-protection (ZnO) or flame retardant ($Mg(OH)_2$) properties. The "ENM (weighted)" bars represent further weighted results according to ENM targeted functionality improvements.*

When assessing according to the adjusted material functionality, meaning that products may be used longer and more frequent, than the PVC-wood outdoor flooring and PS insulation panels for buildings with ENMs do perform better. While for the PP air-condition part for cars and PP garden chair this is not the case, but the difference in impact is small. This comparison, where the functional unit is altered from weight based to material functionality adjusted, means that depending on the LCA approach to define the functional unit ENM material products can become more favourable in terms of environmental impacts – and even in some cases outperform the products that use conventional additives instead of ENMs. Concerning the flame retardancy the avoided human toxicity from DECABDE is several orders of magnitude higher than other impacts from the system even though the ENM product in all other impact categories have a significantly higher impact than the conventional solution. These conclusions are based on an default weighting factor of one, meaning that all impact categories in LCA are considered equal in terms of importance (e.g. global warming is equal to ecotoxicity). Figure 5 shows the overall aggregated results.

1.4 Main dissemination activities and the exploitation of results

The final public dissemination workshop was organized as part of the VI International Conference on Surfaces, Material and Vacuum in Merida, Yucatan, Mexico between 23rd and 24th of September 2013. Within the conference, there was a dedicated symposium for the EU-Mexico cooperation projects called “Adding value to mining products through nanotechnology”. From MINANO project, there were six oral presentations and three poster presentations. The symposium was mainly organized by Oliverio Rodriguez (CIQA/MINANO) and Sandra Rodil (UNAM/BisNano). The symposium was scheduled for two days 23rd – 24th of September 2013. Poster session was in the evening of 24th September.

There were six oral and three poster presentations in the symposium. Oral presentation from Francesco Ferroni (SOVERE) and Benjamin Zamudio (OWENS) were cancelled due to changing employer and due to company internal confidentiality reasons, respectively. Mika Paajanen (VTT) showed the general overview presentation about the MINANO project. Facundo Ruiz (UASLP) talked about the mass production of nanoparticles, Carlos Tena (SAPSA) about the functionalization of the nanoparticles, Carlos Espinoza (CIQA) and Graciela Morales (CIQA) about the PP-nanocomposites and Mirko Miseljic (DTU) about the LCA. Posters were presented by Hannu Minkkinen (VTT) related to wood-plastic composites and Mika Paajanen about UV durability of PP-nanocomposites. Mirko Miseljic showed results about the environmental sustainability of metal nanoparticles.

During the project, special functionalities were developed for plastic and wood-plastic composites by the addition of metallic nanoparticles. Such functionalities included Flame Retardancy, Antimicrobial Protection and UV Protection. Protocols to evaluate the functionalities and regulation to compliance were defined by partners involved in applications. In the case of Flame Retardancy, the functionality was given by the addition of micro and nanoparticles of magnesium dihydroxide to the plastic and wood-plastic composites. The evaluation method for the functionality was the UL94 the standard for safety of flammability of plastic materials for parts in devices and appliances testing antimicrobial protection functionality was provided by the interesting combination of silver and zinc oxide nanoparticles into the plastic composites. The functionality was evaluated according to the Japanese industrial standard JIS Z 2801: 2000, antimicrobial products test for antimicrobial activity and efficacy.
For UV Protection functionality, zinc oxide nanoparticles were added into the plastic and wood-plastic composites. The evaluation of this functionality was performed by the measurement of the percentage of transmittance of the samples.

In summary, applications in PP and wood/plastic composites have not yet been clearly identified by industry. Because of that, potential market is difficult to foresee, as well as environmental and technological challenges that new products will face in the final applications selected. Applications were not defined in proper time to be able to identify the potential market for each product.