

PROJECT FINAL REPORT

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Name of the scientific representative of the project's co-ordinator¹, Title and Organisation:

Tel: +34 91 79120 20

Fax: +34 91 791 21 01

E-mail: antoniojose.sanchez.rojo@acciona.com

Project website^{Error! Marcador no definido.} **address:** <http://www.nanocore-project.eu/index.php>

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

Contenido

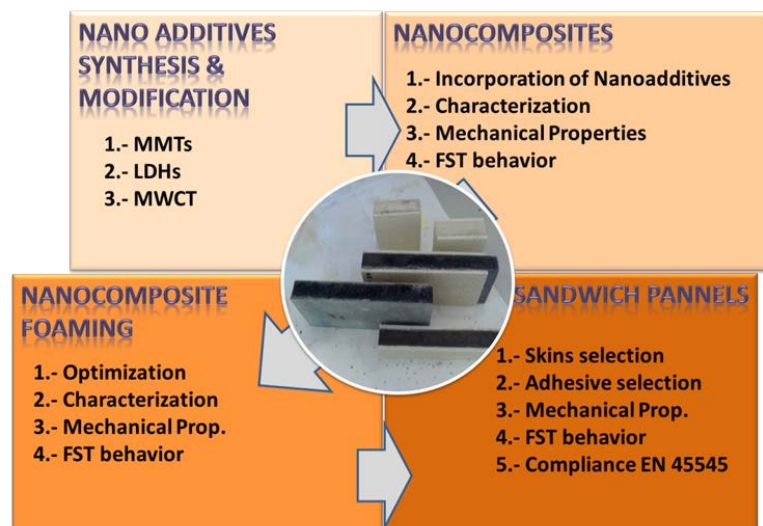
1.	FINAL PUBLISHABLE SUMMARY REPORT	3
1.1.	EXECUTIVE SUMMARY	3
2.	PROJECT CONTEXT AND OBJECTIVES	5
2.1.	Project Context	5
2.2.	OBJECTIVES	6
3.	MAIN S&T RESULTS/FOREGROUNDS (not exceeding 25 pages),	8
3.1.	NANOCORE Project Overview	8
3.1.1.	Introduction	8
3.2.	Project Summary	8
3.1.2.	Towards Objective 1	10
3.1.3.	Towards Objective 2	14
3.1.4.	Towards Objective 3	16
3.1.5.	Towards Objective 4	19
3.1.6.	Towards Objective 5	21
4.	LIST OF DELIVERABLES	24
5.	LIST OF MILESTONES	24
6.	Use and dissemination of foreground	25
6.1.	DISSEMINATION RESULTS (PUBLIC)	25
4.1	Report on societal implications	32
2.	FINAL REPORT ON THE DISTRIBUTION OF THE EUROPEAN UNION FINANCIAL CONTRIBUTION	; Error! Marcador no definido.
Report on the distribution of the European Union financial contribution between beneficiaries		; Error! Marcador no definido.

1. FINAL PUBLISHABLE SUMMARY REPORT

1.1. EXECUTIVE SUMMARY

The NANOCORE (Development of a low FST and high mechanical performance nanocomposite foam core material for ferries and cruise ship superstructures.) Project was a two year EU FP7 project running from 2011 to 2013. It brought together 6 partners from research and development centres and small and medium enterprises from across the EU.

The aim of the NANOCORE project is to develop a technology to modify an existing polymer foam core material by using modified nanocomposites in conjunction with synergistic non-toxic flame retardants, meeting the requirements of the SOLAS regulations and the European REACH legislation. The new foam also have enhanced stiffness, strength and toughness compared to existing materials for the same foam density due to the reinforcing effect of the chosen flame retardant system. A flow chart showing the various stages of the NANOCORE project is shown in the figure below (figure 0).



The effectiveness of the overall NANOCORE solution has been assessed by thoroughly evaluating/testing novel developed foams following the stricter EU standards. All NANOCORE objectives were completed successfully within budget and on time. The research and deliverables from the NANOCORE project have been disseminated widely both locally, in the countries of respective NANOCORE partners and internationally through journal and conference papers and international Fairs. Information from the project has been made available to academia and the polymer-based foam industry.

The major achievements towards the main NANOCORE objectives can be summarized as follows:

- Synthesis of novel organo modified LDHs with improved FST behavior.
- Successful incorporation of nanoclays and MWCNTs to PVC.
- Development of novel polymeric based sandwich panels with enhanced FST behavior.

Overall, the project successfully met all its 8 milestones as specified in the Annex I of the Grant Agreement, delivered more than 20 technical deliverables, published 5 articles in journals and international conferences. Plans for commercial exploitation and valorisation of the project outcomes have been also set.

Contact:

Dr. Javier Sacristan Bermejo
ACCIONA Technological Centre
Valportillo II, 8
28108, Madrid, Spain
Tel: +34 91 791 20 20

Javier.sacristan.bermejo@acciona.com

Detailed information on the project results, the team and all public reports are available on the NANOCORE website <http://www.nanocore-project.eu/index.php>

2. PROJECT CONTEXT AND OBJECTIVES

2.1. Project Context

The introduction of composite materials in the primary and secondary structure of marine vessels increased in the last ten years. In this sense, sandwich constructions are the key factor to build lightweight, reliable and durable vessels. In fact composite materials are being used for boats and ships of ever-increasing size. Yachts over 50 meters and the 70 meter Swedish Visby class corvette are examples of how design and fabrication methods have improved. However, unlike steel and aluminum, composite materials are combustible during shipboard fires.

Fire safety is one of the main driving forces that lead to regulatory agencies to establish limitations on the size of vessels that can be built with composite materials. Polymeric resin systems have the greatest influence over how a laminate will perform in a fire. In case of a fire the polymer-based sandwich constructions will be exposed to the tough natural forces of a fire. Temperatures can be as high as 1000°C, smoke can be created in large amounts and the structure of the ship can be weakened.

In fact, smoke during a fire can be the biggest problem on a ship, much as it is in building fires. Most fire fatalities are from carbon monoxide poisoning. Visibility during fires is also an issue, both for people trying to evacuate and fire-fighters trying to extinguish the blaze. Some composites will burn “blacker” than others, although the source of the fire and other furnishings produce an overwhelming amount of smoke on their own. In addition there also has been some concern that fire retardant additives may have toxic properties during fires, but carbon monoxide exposure seems to override all other threats.

From all of this it is clear the impact that developing new high performance foam core sandwich composites will have not only in marine applications but also in railway and construction markets.

Now, regarding the use of composite materials for construction each industry, recreational, commercial and naval maritime industries all have different regulations. Regulations vary with fire threat; size and complexity of the vessel; ship operational parameters; risk to passengers and crew; and liability issues. As regulatory agencies move towards “performance based” standards, fire test methods are often cited in lieu of specifying certain allowable materials. Small-scale test methods afford the greatest level of scientific sampling while large-scale tests simulate actual fires and synergistic effects of material systems. For the development of novel materials in this market it is necessary to meet the European requirements and achieve low Fire, Smoke and Toxicity (FST) tests values, according to SOLAS (Safety of Life at Sea) regulation. In this work the fire behaviour of composites may be evaluated from standard reaction-to-fire tests, which measure ignitability, flame spread, heat release and generation of smoke and toxic fumes. Further to current fire safety specifications, there are some regulatory developments in Europe that are challenging composites in future. The EC Construction Products Directive has defined Essential Requirements in terms of fire safety. These requirements in the area of reaction-to fire have been implemented by the

establishment of 6 Euroclasses. These trends in regulations and standards have emphasized the need to ensure that composites are tested in end-use conditions.

In addition and more closely related to this project, many transport applications are regarded as high risk ones in relation to fire safety. There is increasing concern about the generation of heat, smoke and toxic gases from polymers and composite components used in, for example, trains, ships and aircraft. Some regulations are already in place for ships; this trend is likely to continue and will be refined as tests improve. Furthermore, European railway directives have recently been published concerning interoperability of trains across the EU and new fire classifications will be required for products installed in future European trains.

In this regard many of the recent developments concerning fire safety regulations and standard test methods for composites have been driven by the following organizations:

- a) ISO, IEC, CEN and CENELEC
- b) Regulators such as the EC (Construction Products Directive, Marine Equipment Directive), IMO (SOLAS), FAA, etc;
- c) Transportation manufacturers and operators such as Boeing, Airbus, LUL, NCF, etc.

In this Project all materials were evaluated following the new standard CEN 45545. It is important to realize that new changes are on-going in the railway industry to standardize the regulation in order to guarantee the same level of security whatever the location in the EU. These new trends imply key changes in the material development approaches that involve products with a low kinetic of degradation. This implies the use of new fire-retardant chemistry and opens the space for a new generation of solutions, although there is still work to be done for other polymeric applications.

The main aim of the NANOCORE project is to develop a technology to obtain a polymer foam core material by using modified nanoparticles in conjunction with synergistic non-toxic flame retardants, meeting the requirements of the SOLAS (Safety of Life at Sea) regulations and the European REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) legislation. The new foam will also have enhanced stiffness, strength and toughness compared to existing materials for the same foam density due to the reinforcing effect of the chosen flame retardant system.

2.2. OBJECTIVES

The successful outcome of the NANOCORE project is dependent on achieving a set of scientific objectives to provide us with the knowledge needed to develop the technology to meet the project's technological and commercial goals. In particular, the overall scientific/technological objectives of NANOCORE project were:

1. Development of nanoparticles with phosphorous based compounds grafted onto the surface of the particles.
2. Development of a process where nanoparticles are dispersed in the polymer by mechanically mixing them into the molten polymer prior to foaming without affecting the ability to mould the polymer and where nanocomposite agglomeration is reduced to less than 5%.
3. Development of a PVC based polymer containing modified nanoparticles which can be foamed using existing processing equipment; the viscosity of the PVC polymer containing nanoparticles prior to the foaming process will not exceed a 10% of the base polymer.
4. Development of a PVC based foam incorporating less than 10% (w/w) of the developed nanocomposite particles with enhanced strength and stiffness at least 10% greater than the equivalent density of the unmodified foam.
5. Development of a PVC based foam in which modified nanoparticles provide low Fire, Smoke and Toxicity (FST) values.

In order to reach these objectives, the consortium has reached important scientific improvements and innovations over existing PVC based polymer foam core materials that involve:

- Improved compatibility of nanoparticles platelets with the polymer foam matrix.
- Improved distribution of phosphorous based FR compounds within the foam.
- Reduce loss of phosphorous based FR during processing.
- Lower weight percentage of FR in the foam.
- Refinement of the foam microstructure.
- Increased specific mechanical properties of the foam due to smaller cell size.
- Increased specific mechanical properties of the foam due to nanoparticles reinforcement.

* The improved thermal stability in polymer nanocomposites is due to the effect of nanoparticles platelets which hinder the diffusion of volatiles and assist the formation of char after thermal decomposition.

- Improved Fire Smoke and Toxicity properties due to synergistic effect of phosphorous based FR materials and the FR properties of nanocomposites.*

*Flame retardancy and mechanical properties are both improved in clay-based polymer nanocomposites while the mechanical properties are always degraded in polymer composites with conventional flame retardants.

Our integrated performance objectives for the production of the NANOCORE new material are:

- The foam will be formed into the desired end shape by moulding.
- The production cost to be €25/kg and the end user cost €40/kg
- Repeatable product quality of < 5% variation
- Reduce energy consumption and CO2 emissions during foam production by 10%

3. MAIN S&T RESULTS/FOREGROUNDS (not exceeding 25 pages),

3.1. NANOCORE Project Overview

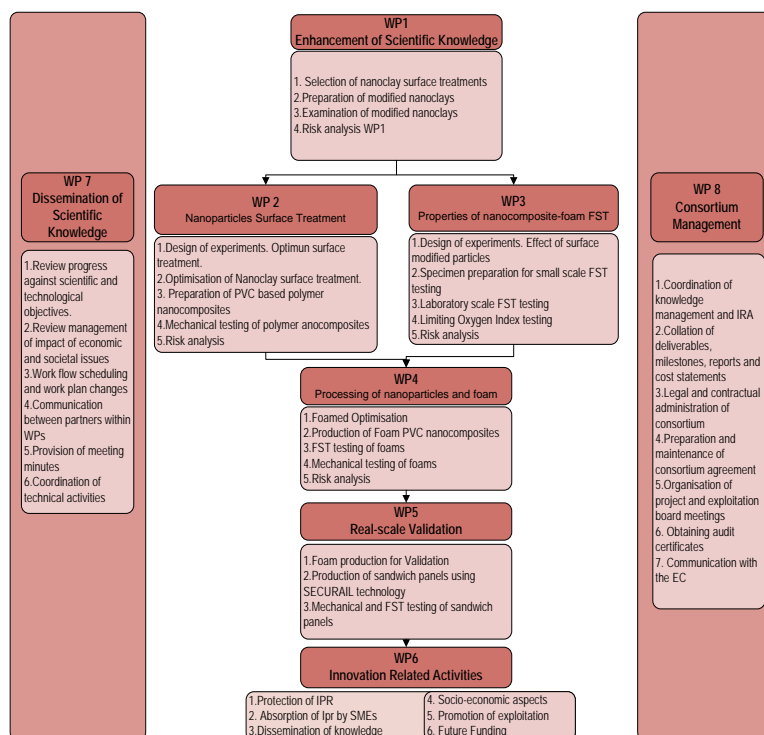
3.1.1. Introduction

The NANOCORE Project started in September 2011 and after duration of 24 months finished in September 2013. It brought together 6 partners from research and development centres and small and medium enterprises from across the EU: ITA (Spain), CGS (Italy), AP&M (Portugal), Plasticos Karey (Spain), Glonatech (Greece) and ACCIONA (Spain).

Several tasks have been undertaken by the different work packages and the different partners composing the NANOCORE project. Below, we present a short summary with the main scientific and technical results achieved with respect to the above major objectives of the project. More details can be found in corresponding NANOCORE deliverables and publications listed on NANOCORE website.

3.2. Project Summary

The activities of NANOCORE project were organised by adopting a Work package (WP) structure according to the following subdivision see figure below (PERT NANOCORE):



For developing NANOCORE solution, as first activity, a survey of current regulations and standards were compiled in order to establish for the rest of the project the FST and mechanical test procedures, values to be met and prohibited compounds. This survey was complemented by a scientific literature review with respect to prior work on the surface modification of nanoparticles for its incorporation in polymer materials identifying phosphorous based onium compounds that may potentially lead to novel organo modified nanoclays with enhanced fire retardant properties and low smoke production. Based on this analysis, the most promising surface treatments were selected and new samples were prepared using these treatments.

On the basis of these results several surface modification treatments for nanoparticles (montmorillonites and layer double hydroxides) were developed which will presumably improve the fire, smoke, toxicity and mechanical properties of the foams. The nanoparticle modification procedure was optimized, using 7 different types of modification agents. Test samples of polymer nanocomposites consisting of surface modified nanoparticles dispersed in PVC were successfully produced by melt blending. First series of FST and mechanical tests were carried out on samples with loads of 5 and 10% by weight of the nanoparticle.

These activities were performed under the WP1 and the related outcomes represented a relevant input to the activities of the WP2 and WP3, regarding the nanoadditive modification methodology, nanoadditive dispersion procedure and characterization and FST and mechanical tests, and WP4 concerned with processing of nanoparticle and foam and WP5 validation of NANOCORE technology following EN 45545 standard.

The scientific pillars at the basis of the NANOCORE solution were two: the modification of nanoadditives to prepare FR polymer-based nanocomposites and the foaming of nanocomposites.

Therefore, WP2, WP3 and WP4 were specifically devoted to the development of new organo-modified nanoadditives, improvement of the existing ones and evaluation of FST and mechanical properties of the novel nanocomposite foams.

3.1.2. Towards Objective 1

Development of nanoparticles with phosphorous based compounds grafted onto the surface of the particles.

The main aim from NANOCORE was the development of polymer foams from PVC that will serve as the core of sandwich structures. The foam is enhanced with modified nanoparticles consisting of either a two-component flame retardant system (Layered-Double-Hydroxides(LDHs) or montmorillonites (MMTs)) in conjunction with synergistic organophosphorous compounds) or high-purity multi-wall carbon nanotubes (MWCNTs).

Sodium montmorillonite (abbreviated as MMT) was first selected as the candidate nanoparticle type for the FR system. This natural occurring material is composed of anionic charged layers of silicate that are counterbalanced of sodium cations in the interlayer region. Through a direct exchange reaction, these cations can be chemically replaced with others such as phosphonium compounds, and this will provide new properties to the surface that will later enhance nanocomposite quality due to nanoparticles homogeneous dispersion

Phosphorus-based products are known as flame retardants. Typically, phosphorus based flame retardant is designed to develop its activity in combination with the starting decomposition of basic polymer. It can offer a partial gas phase contribution to the flame extinguishing effect which is comparable to brominated flame retardants. However, the main feature is char forming activity sometimes combined with foaming or intumescences, which forms a protective top layer on the surface. This type of solid phase mechanism provides an advantage of less release of smoke and gases in case of fire situation.

Seven different omniun compounds were initially selected. The phosphonium compounds were chosen in order to study the difference of the modifier structure in the final properties of the organoclays.

The first group selected P1, P2 and P3 are water soluble and the counter ion is bromide. Main differences among these come from the phosphonium compound with phenyl groups.

The second group P5, P6 and P7 correspond to alkyl phosphonium molecules with 3 different anion species. These compounds are not water soluble and therefore it was necessary to disperse them in a water/ethanol mixture in order to obtain the most favourable dissolution of the sample.

P1: A triphenyl phosphonium structure with a short methyl group attached, P3: also a triphenyl phosphonium structure but with a longer alkyl chain (4-carboxybutyl), P2: A tetraphenyl phosphonium group with more aromatic content and Dim: A dimeric structure with a bis-phosphonium group.

P4, P5 and P6 correspond to alkyl phosphonium molecules with the alkyl chain trihexyl(tetradecyl) phosphonium and 3 different anion species: bis(2,4,4-trimethylpentyl) phosphinate, bromide and decanoate.

Therefore we follow two different approaches:

a) *Surface modification of Montmorillonite nanoclay particles in aqueous solution.*

This process is applied to the water soluble phosphonium compounds P1, P2, P3 and Dim. Pristine montmorillonite (MMT) filled with sodium cations, Cloisite® Na⁺, was used as the precursor nanoclay. The surface treatment takes place through a direct cation exchange reaction based on the protocol developed by Patel et al. The exchange reaction occurs rapidly as the phosphonium compound is added to the solution, and a white and bulky solid is produced. The product obtained was then next dried at 110°C overnight. Finally, the dried organoclay is milled using an agate mortar to reduce the particle size.

b) *Surface modification of nanoclay particles in ethanol-water mixture.*

In the case of P4, P5 and P6 phosphonium compounds, that are water insoluble, the procedure applied for the surface modification of the pristine montmorillonite (Southern Clays, Inc) was based on that described by Jin Uk Ha in which a more organic solvent is employed. Phosphonium compounds are dissolved in the stoichiometric amounts of the CEC of the nanoclay in a mixture of EtOH: H₂O (proportion 70:20) during 10 minutes with continuous magnetic stirring. When dissolution is completed, Cloisite® Na⁺ is added and the dispersion is heated up to 70°C. Finally, the organoclay is dried at 110°C overnight and milled with an agate mortar as described for the former water soluble samples.

In order to confirm that the surface modification of the nanoclay had taken place, several techniques were applied. Thus, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and powder X-ray diffraction (P-XRD) were used to the characterization of the prepared organoclays.

From Fourier transform infrared spectroscopy (FTIR) spectra, the most important evidence about the successful cation exchange process is obtained when comparing NaMMT (Cloisite® Na⁺) spectrum with that of the organically modified clays and the pure phosphonium compounds. In the case of P1, P2, P3 and DimMMT (see Fig.3 (a)) the spectra showed the appearance of new bands in the range of 800-650 cm⁻¹ that are characteristic of the bending vibration modes of the aromatic rings (associated to the phenyl groups in the phosphonium ions). For P4, P5 and P6MMT (see Fig.4 (a)) it can be observed new bands near 3000 cm⁻¹ which are related to the stretching vibration mode of the Csp³-H bonds (produced by the alkyl chains in the phosphonium. ions).

In conclusion, FTIR analyses of the solid samples show that the organic modification of the montmorillonite has been successfully carried out.

Results from **Wide angle X-ray diffraction (WAXD)** on dried powder samples provides information regarding the basal spacing change between layers after exchanging sodium ions with the phosphonium cations. The intercalation of the organic phosphonium molecules in the interlayer space causes a shifting of the $\langle 001 \rangle$ reflection to lower 2θ values as can be observed in the Figure below. The basal spacing increases due to the surface modification of the clay. For example, the modified nanoclays P2MMT, P3MMT and DimMMT have a basal spacing of 1,8 nm, which is 1,6 times the spacing of NaMMT. Regarding the compounds produced in water/ethanol solution (P4MMT, P5MMT and P6MMT), the interlayer increase is not as high as in case of modification from water soluble phosphonium species (about 1.7 nm).

The increased basal spacing of all synthesized phosphonium-MMT species indicates that the larger phosphonium cations enlarge the interspacing by replacing the sodium ions of MMT. Therefore, it can be concluded that the cationic exchange of nanoclay and consequently its surface modification has been successfully carried out.

Thermogravimetric analyses (TGA) of the dry milled samples were made in order to obtain quantitative data about the accomplishment of the surface modification of the clay.

Weight loss of the pristine montmorillonite (NaMMT) takes place in three main steps, a) free water/dehydration, b) decomposition of organics and c) dehydroxylation.

From these experiments, it can be concluded that different thermal behavior is obtained for each surface treatment and also for each pure onium compound. In the pristine state, the most thermally stable phosphonium compounds are P1 and P2 since they reach the higher temperature at which a weight loss of 5 or 10% occurs. When considering the organoclay, the samples P1MMT and P2MMT also present the higher thermal stability. This can be explained due to their higher aromatic content in comparison with the other phosphonium compounds

Modification of layered double hydroxide (LDH) nanoparticles with phosphorous compounds

A second strategy of nanoparticle surface modification was addressed. The compounds selected were Layered Double hydroxides (LDH), well known as chloride scavengers which in principle should contribute to retard dehydrochlorination of PVC. Unlike the MMT nanoparticles, the LDH are anionic and therefore the phosphorus compounds selected for exchange have to be negatively charged as well. Different kinds of additive and reactive flame retardants containing phosphorus are increasingly successful as halogen-free alternatives for various polymeric materials and applications. Phosphorus can act in the condensed phase by enhancing charring, yielding intumescence, or through inorganic glass formation; and in the gas phase through flame inhibition. Phosphate ester FR products include triphenyl phosphate or TPP, resorcinol bis (diphenyl phosphate) or RDP, and bisphenol A bis(diphenyl phosphate) or BDP. These three phosphorus FR products contribute the largest volume share of this product group.

Following these statements, we have selected several phosphate derivatives with similar structure as the commercial ones with at least one negative charge in order to chemically modify the LDH-CO₃ precursor. SDS (sodium dodecyl sulphate) and BEHP (bis(2-ethylhexyl)phosphate) were

reported as novel modifiers of layered double hydroxides by F. R. Costa et al., and were chosen to compare them with another surfactants; SDP(sodium dodecyl phosphate) and PET11 (Poly Aryl Ether Phosphate).

Surface modification of LDH particles: regeneration method

Surface modification of layered double hydroxides takes places through the regeneration method, as was described by F. R. Costa et al.. The procedure consists of several steps; basically, carbonate anions and water are eliminated from the structure, through calcination. Then the calcinated LDH is added to an aqueous solution of the surfactant and after several hours, the solid is recovered by filtration, washed, dried and finally milled in order to get a fine and white powder. The result of the modification protocol was tested by means of FTIR and XRD. From FTIR, it can be observed the typical bands characteristic of the bending vibration modes of the aromatic rings present in the modifying compounds, the phosphine, phosphonate and sulfonate bands.

As expected the interlayer spacing determined by means **of XRD** between clay layers after the modification reaction increases with the different phosphorous reactants indicating a successful incorporation of the selected compounds between the LDH layers. The basal spacing increases in the following order, BEHP, DPP, SDS, SDP and PET11. It goes from 0.76Å up to 6.6 Å indicating clearly that the corresponding surfactant can be found between LDH layers.

Looking at a future industrialization stage, a key issue in the nanoparticles modification will be the preservation of properties after up scaling. With this purpose, some experiments were conducted using ten times more batch size in order to compare with the samples prepared in lower quantities.

The main results obtained from XRD indicate that the increase in batch size from the samples P2MMT, P3MMT and DimMMT does not modify the interlayer distance obtained in the cation exchange reaction. When examining the samples produced in water/ethanol mixture, (samples P4MMT and P6MMT), the WAXD results one can observe a broadening of the peak corresponding to the higher quantity compound, and a slight displacement of the reflection peak to lower 2Θ values, indicating that the basal spacing has increased.

From all these experiments, it can be concluded that the surface modification of cationic and anionic nanoclays with several types of phosphonium and phosphorous compounds respectively, has been successfully carried out and there is a large palette of fire retardant compounds available to be incorporated in pristine PVC.

It is worthy of mention, that pristine MWCNTs and modified MWCNTs with (amino, phenol and carboxylic groups) were provided by GLONATECH (NANOCORE SME partner). Modification procedure is confidential.

3.1.3. Towards Objective 2

Development of a process where nanoparticles are dispersed in the polymer by mechanically mixing them into the molten polymer prior to foaming without affecting the ability to mould the polymer and where nanocomposite agglomeration is reduced to less than 5%.

Polymer nanocomposites, consisting of a polymer matrix with nanoparticle filler, have been predicted to be one of the most beneficial applications of nanotechnology. Much research has focused on the preparation and thermal and mechanical characterization of nanocomposites. However, mainly due to the varying polymer matrix/filler systems and varying preparation techniques is not easy to establish a clear trend in nanoparticle performance. In general, nanocomposites showed great improvement of mechanical and FST properties over those of micro-filled composites.

Despite this recent proliferation of nanoclays as additives for polymers in academic research and, to a lesser extent, in industrial practice, high performing clay-reinforced nanocomposites based on poly(vinyl chloride) (PVC) have remained elusive. An important limitation in the use of PVC derives from its weak resistance to fire and thermal degradation in general. Under the effect of temperature, PVC exhibits a fast degradation associated with the release of chlorine and hydrogen as the most important volatile products. These gases can interact resulting in a high local concentration of HCl which is considered toxic & irritant a relatively low concentration. Through the incorporation of organo-modified nanoclays and/or CNTs we not only try to enhance FST behaviour but also retard the thermal degradation of PVC.

A critical factor in nanocomposite properties is the dispersion of the nanoparticles in the polymer matrix. Dispersion of inorganic nanoparticle filler in a thermoplastic is not easily achieved because nanoparticles have a strong tendency to agglomerate to reduce their surface energy. Several approaches have been used until now to produce better dispersion, melt intercalation, grafting polymers to surround nanoparticles, adsorbed polymers to sterically stabilize nanoparticle dispersions limiting formation of flocculants and aggregates, and in-situ polymerization among others. Although the studies presented above utilized a wide range of sample preparation techniques, no technique proved significantly better than any others.

In our case, taking into account that the project is industrially oriented and the most usual processing method for PVC is extrusion (high shear dispersion method), PVC nanocomposites were prepared by melt mixing in an internal mixer with a chamber volume of 60 cm³, Haake-Rheomix 9000 equipped with a pair of high shear roller type rotors. The composites were prepared to three filler concentrations (2.5, 5 and 10 wt.-%). Subsequently, the samples were compression-molded in a Collin P200P electrically heated hydraulic press at 180 °C for 5 minutes (3 min. at a pressure of 10 MPa and 2 min at 150 MPa) and a cold press for 2 min. at 150 MPa.

Firstly, the optimal processing conditions were determined, varying different process parameters: temperature, time, rotor rate, and order of incorporation of ingredients (PVC formulation and filler).

Final parameters selected were: Temperature 150-165°C, rotor speed 100rpm and mixing time1 10-15min, time2 (blowing agent) 5-10min.

The filler was mechanically mixed with the PVC resin formulation before it was added to the internal mixer. However, in order to improve the dispersion of the filler in the PVC matrix, it would be more appropriate to carry out the dry blending of PVC/nanofiller with other additives of the formulation in a high intensive mixer before feeding the internal mixer.

On the basis of scanning electron microscope (SEM) analysis (to evaluate dispersion degree), and TGA (to evaluate thermal stability) the processing window for preparing the composites was established. From a visual inspection of PVC nanocomposite sheets, the images revealed a very homogeneous aspect where the fillers are not visible to the naked eye. This suggests, at least from a qualitatively point of view, that the processing method is effective for preparing PVC composites.

Obviously the “naked eye” is not enough to guarantee nano-clay dispersion degree within the PVC matrix. In general, the degree of dispersion of the clay platelets into the polymer matrix determines the structure of nanocomposites. Depending on the interaction between the clay and the polymer matrix, two main idealized types of polymer–clay morphologies can be obtained: namely, intercalated and exfoliated. From a practical point of view an exfoliated structure results more interesting and possess better properties because the individual silicate layers are completely separated and dispersed randomly in a polymer matrix.

WAXD analysis and transmission electron microscopy (TEM) observation are generally the two methods that have been used to typically establish the structure of nanocomposites. In principle, conclusions based solely on WAXD patterns are only tentative when concerning the mechanism of nanocomposite formation and their structure. XRD analyses of composite showed that some intercalation of the polymer was produced because the diffraction peak was shifted to lower angles (indicating that the separation of the layers had increased). TEM allows a qualitative understanding of the internal structure, spatial distribution of the various phases, and views of the defect structure through direct visualization.

On samples containing unmodified MMT dispersion of the filler is not good because big agglomerates predominate with some other finer particles both at 5% and 10% of nanoparticles concentration. The integrity of the layers remains in the composites and its regularity has not been disturbed by the polymer, what points to that exfoliation has not been produced and the process that has taken place has been at most intercalation, which is also reasonable because of the hydrophilic nature of the montmorillonites.

From the organic modification of the montmorillonite it is expected a better dispersion of the nanoparticles because of the chemical similarity between the polymer chains of the matrix and the organic modifier. This compatibility would result in an intercalation of the polymer between the silicate layers and, in the best case, in its exfoliation into single layers. Previous XRD analyses of PVC MMTP6 nanocomposite showed that some intercalation of the polymer was produced because the diffraction peak was shifted to lower angles.

By TEM analysis it was possible to observe the layer pattern of the montmorillonite, which showed parallel layers of silicate in most of the cases, indicating only the intercalation of the PVC chains and not exfoliation. In the case of 5% of filler loading, exfoliation was observed in some parts of the material (at 60000X magnifications). In terms of dispersion of the nanoparticles, TEM images reveal some areas of the material with better dispersion in the case of the composite with 5% of filler compared with the unmodified MMT, with little agglomerates, but in the case of the 10% concentration agglomerates are in the order of several microns although in some parts particles show good dispersion.

This result is very similar in all the samples containing MMTs.

Nanocomposites containing unmodified LDH, follow a similar trend to the previous samples. In some parts of the composite good dispersion of the LDH particles could be found (image at 5000X) but in other parts big aggregates are formed, indicating poor dispersion of the filler. This situation improves upon modification of the LDH leading to a better dispersion and in some cases close to exfoliated structure.

Finally nanocomposites containing MWCNTs, display the best dispersion, independently of the chemical modification (pristine, amine, phenol or carboxylic). In both cases, 5% and 10%, from TEM images one can see a high dispersion of the particles in the polymer. MWCNTs are relatively well dispersed in the PVC resin. However in the more concentrated sample, some “islands” of MWCNTs can be observed that in the sample because agglomeration.

In general, the nanocomposites containing pristine and modified MMT and pristine LDH presented an intercalated structure. The best situation is noticed when the filler corresponds to multiwall carbon nanotubes (MWCNT) where the nanocomposite showed a good exfoliated structure. Nevertheless, in this case one can detect some aggregates in the structure, which can strongly affect the mechanical properties of the nanocomposites. It is also known that exfoliation is an advantage for mechanical properties. However, there appears to be no difference between intercalated and exfoliated polymer–clay nanocomposites for fire properties.

3.1.4. Towards Objective 3

Development of a PVC formulation containing modified nanoparticles which can be foamed using existing processing equipment; the viscosity of the PVC polymer containing nanoparticles prior to the foaming process will not exceed a 10% of the base polymer.

Polymer nanocomposite foams, polymer foams with nanoparticles, are an intriguing class of materials with unique structure and properties. Nanoparticles not only improve mechanical performance of the hosting material but also are able to add new functionalities to polymer foams.

Polymer nanocomposites offer an exciting opportunity in the formation of polymer foams for four key reasons:

- 1.- The nanofillers act as heterogeneous nucleation sites.
- 2.- Nanofillers can provide multifunctionality.
- 3.- Nanofillers change the rheological properties.
- 4.- The shape, size and surface chemistry of nanoparticles can be tailored to control the foam structure, and therefore, foam properties.

Polymer foams are made up of a solid and gas phase mixed together to form a foam. The gas that is used in the foam is termed a blowing agent, and can be either chemical or physical. In this work, following recommendations from one of the industrial partners, Plásticos Karey, two different chemical blowing agents were tested, Expancel® and azodicarbamide. In addition, in order to optimize, chemical blowing agent concentration and plasticizer type and content six different PVC formulations (provided by Plásticos Karey) were also tested.

From the first set of results is clear that both nanoparticle and CBA concentration play the dominant role on the expansion ratio of the final PVC foams. As observed by SEM formulations containing Expancell lead to more compact and dense foams than with azodicarbamide. This is mainly due to the fact that the processing/expansion temperature selected is few tenths of degrees lower than the maximum expansion temperature recommended for Expancell because processing temperatures higher than 180°C would contribute to PVC degradation.

So taking into account these results and PVC processing “limitations” it was found that the most suitable and best performance blowing agent according to the processing method selected was azodicarbamide which was combined with a phthalate free plasticizer allow NANOCORE to fulfill REACH regulations.

The foaming conditions are the major determinants of final polymer foam morphology. The effects of temperature on the foaming of PVC nanocomposites were also investigated.

It was found that influence of temperature on foaming performance it is more important on formulations with Expancell because it requires a higher decomposition temperature than with AZC. At the lowest processing temperature, 170°C, foam expansion degree is about a 10-15% lower and the final density is slightly higher than in the other samples processed at higher temperatures. In addition, pore distribution and size is more heterogeneous and some large pores can be observed. In general, increasing temperature produces a better foaming, leading to a more homogenous pore distribution.

It has been showed that once the optimum decomposition temperature for AZC is reached foam density and the expansion ratio remain quite similar.

Next we look at the influence of nano-additive type and loading degree on PVC foam morphology. The effect on the PVC foaming by the modified nanoparticles was studied by investigating their influence on foam microstructure. The relationship between the quantity of nanoparticles and the resultant foam characteristics was determined and the distribution of the nanoparticles within the polymer constituent of the foam was investigated and quantified. Several samples were characterized by SEM.

Visual observation of the SEM images clearly shows the difference between the foam morphologies of nanocomposites containing MWCNTs and LDH_BEHP nanoparticles to that of pristine PVC. At low and high concentrations of nanoparticles, the foam morphology (average cell size, cell density) present important differences to that of neat PVC which can be in part explained because the nucleation mechanism between these two types of samples are somewhat different: in neat PVC it tends to be more homogeneous versus fully heterogeneous in filled PVC. In this sense, all four samples containing nanoparticles have remarkably low (average) cell sizes and high cell densities.

The cell size measurements of the samples containing LDH-BEHP nanoparticles and CNTs showed that these samples have comparably lower average cell diameters. However, the high standard deviation in neat PVC and nanocomposites containing nanoparticles indicate the presence of a wide distribution of cell sizes in these samples. Previous studies reported that homogeneous nucleation leads to a wide cell size distribution whereas heterogeneous nucleation leads to a narrow cell size distribution. This similarity in the cell size distribution between foamed neat PVC and PVC nanocomposite samples is attributed to the fact that all of these samples had high percentage of heterogeneous nucleation. Nanoparticle containing samples additionally had a second source of heterogeneous nucleation; however this secondary mechanism must have been quite ineffective due to the similarities in the foam morphologies between both set of samples.

In general the addition of nanoparticles lead to foams with smaller cell size. Nanofillers act as heterogeneous nucleation sites while traditional fillers also act as heterogeneous nucleation sites, the small size of the nanofillers means that at a given concentration, there are more of them per unit volume, which creates a larger number of potential nucleation sites but this is tempered by reduced nucleation efficiency. This ability to control the size of cells is important because cell size and cell density can impact the properties of the foam significantly.

New PVC nanocomposite foams have been developed. These foams enjoy highly desirable features easily controllable by nanoparticle type and concentration. They are intended for use in many different practical applications, such as, railway, maritime and construction structures among others.

At the end PVC based foams with a weight fraction of nanoparticles below 10%, have mechanical properties at least 10% higher than that of the un-modified foam and lower FST values were obtained.

3.1.5. Towards Objective 4

Development of PVC based foam incorporating less than 10% (w/w) of the developed nanocomposite particles with enhanced strength and stiffness at least 10% greater than the equivalent density of the unmodified foam.

After successfully manufacture PVC nanocomposite foams (NANOCORE) with controlled density and nanoadditive loading degree the next step was to evaluate their mechanical properties. In fact this had been done previously (WP2) in PVC nanocomposites (before foaming). It was found that samples containing modified LDHs, such as PVC2-SDS and PVC2-BEHP at 5 wt% of nanoclay loading show higher values, up to 25% on the Young modulus compared to pristine PVC2. Addition of either pristine MMTs or LDHs, have a positive effect in tensile strength, it increases up to 10% with respect to pristine PVC1. Further addition of nanoclay (from 5 to 10% in weight) does not seem to induce any other improvement in mechanical performance. However, taking into account that the main objective of NANOCORE is developing PVC nanocomposite foams with enhanced FST and mechanical properties with respect to pristine PVC foams, the next objective was to evaluate the most relevant mechanical properties for polymer foams.

In this work we focus on two of the most relevant properties of polymer-foams, Shear Properties of Sandwich Core Materials and Compressive Properties of Rigid Cellular Plastics. Tests were carried out following ASTM C273 and ASTM D 1621 respectively. The following main achievements are presented with respect to this objective:

1.- Nanocore PVC foams containing pristine LDH, showed up an increment in compressive strength and modulus up to 60% compared to pristine PVC foam.

Samples with 2,5 wt.% concentration of nanoparticles showed the largest increase, up to 60% in the compressive modulus and 20% in compressive strength (PVSK6-LDH-0,9) but as the nanoparticle content was increased further only small enhancements are reached.

2.- In Nanocore PVC foams containing LDH-SDP both the compressive modulus and strength are higher for nanophased foam; there are two different effects, firstly the LDH3 content, addition of only 2.5 wt.% of LDH3 into the PVC foam increases its compressive modulus and strength about 40% and 20%, respectively (0.6 gr cm⁻³).

In this case the effect of nanoclay concentration is less relevant than final density on the values of compressive moduli. In these samples incorporation of small quantities (2,5%) of modified LDH3 to pristine PVC, produces large increments on compressive strength and modulus up to 60 and 150% respectively compared to pristine PVC foams(0.9 gr cm⁻³).

3.- In Nanocore PVC foams containing LDH-BEHP both the compressive modulus and strength are higher for nanophased foam; PVC/LDHBEHP-2,5%-0.6 shows highest and PVCK6/LDHBEHP-5%-0,9 shows lowest. The addition of only 2,5% of LDH4 led to 50% increase in the compressive modulus and 104% increase in the compressive strength (at a density of 0.6), further addition of LDH-BEHP do not improve either the compressive modulus or strength, which might be due to the poor dispersion of some nanoparticles.

4.- In NANOCORE foams loaded with CNTs, the addition of only 2,5% increased the compressive modulus by >150% and the compressive strength by 100% compared to pristine PVC foam. The effect of density on compressive properties is not surprising, both compressive modulus and strength increased up to 100% going from 0,6 to 0,9 gr cm⁻³ samples.

In general, the mechanical properties of polymer foams not only depend on the mechanical properties of the matrix material, but also depend on the density (or the relative density) of the foam and the foam structure (size and size distribution of the bubbles).

Under the same foaming conditions, the NANOCORE foams filled with MWNTs showed greater compressive modulus and compressive strength values than the PVC foams filled with nanoclays. The higher strength of nanophased foams may have attributed from creation of multiple crack sites and/or multiple crack branching due to the presence of nanoparticles into the polymer which delayed the fracture processes in nanocomposites. Another reason for improved strength of nanophased foams is the stronger interface.

In some cases, (LDH3 and 4) further addition of nano-additives does not improve either the compressive modulus or strength, which might be due to the poor dispersion of the nanoparticles.

By design, sandwich cores experience primarily shear stress. Consequently, **shear properties** are among the most important criteria governing the selection of core materials for sandwich structures.

1.- Shear strength of nanophased foam was higher than that of neat. At the initial stage of loading small cracks were noticed in the core near the edge of the specimen. As the loading continued, the specimen elongated, small cracks coalesced into a dominant crack, and kinked into the core. Crack formation and propagation were identical with both categories of foams, but elongation with nanophased foam was higher.

The largest improvement on shear properties is achieved on samples with only 2,5 wt% of CNTs. It has also been reported that the addition of multi-walled carbon nanotubes could increase the compressive modulus and strength of thermoplastic foams significantly not only because of the reinforcement of the matrix by MWNT, but also because of the reduction of cell size due to heterogeneous nucleation at the MWNT surface.

3.1.6. Towards Objective 5

Development of a PVC based foam in which modified nanoparticles provide low Fire, Smoke and Toxicity (FST) values

The principal objective of NAOCORE is to manufacture PVC nanocomposite foams with enhanced **Fire, Smoke and Toxicity** performance. To this end NANOCORE foams were thoroughly tested in a cone calorimeter following standard CEN 45455. The following main achievements are presented with respect to this objective:

Cone calorimeter yields information on the heat produced by the combustion of materials under the impact of an external radiation. The interpretation of heat release curves follows the following, straight forward pattern:

- The later ignition occurs, the better
- The lower the heat release rate, the better
- The lower the integral value, the better
- The later a significant heat release occurs, the better

Among all the information that can be extracted from these tests, results of foamed PVC nanocomposites are discussed putting special attention on three parameters, ignition time, FIGRA index and fire performance index (FPI).

The **ignition time** (tig) is defined as the time at which a continuous flame is supported on the material surface. A larger time to ignition would mean better fire retardant performance.

The **FIGRA** (Fire Growth Rate), namely the ratio between the immediate Heat release rate value and the time during which this value is recorded, plays an important role in classification. *Lower values would indicate less fire hazard.*

The total fire performance of a material can also be understood from the fire performance index (**FPI**), which is the ratio between the time of ignition (time) and the peak rate heat release (PHRR). It is suggested to be related to the time to flashover, i.e. change from small to large-scale fire (or time available for escape) in a real fire. Thus it may be considered to be the best individual indicator of overall fire hazard. *Higher values of FPI indicate less fire hazard.*

Ignition temperature (Tig) has been investigated under radiative heating for different polymers by several authors and is generally reported to be practically independent of imposed heat flux for non charring polymers, whereas decreasing with increasing irradiance was reported for charring polymers such as natural cellulosic polymers.

In NANOCORE once nanoclays either LDHs or MMTs and MWCNTs were mixed with pristine PVC and foamed, some of the nanocomposites foams shown lower ignition times which might be attributable to an initial combustion of phosphorus moieties before these could perform as

fire retardants but in other samples the modification lead to larger ignition times of about 30%. So, the effect of nanonclay content and type on ignition times is somewhat unclear. In general is well-known that presence of nanoclays at least modified FST performance of the polymer nanocomposite.

For polymer/layered silicate nanocomposites (similar to NANOCORE samples), variable trends for time to ignition have also been reported: a reduction of TI compared to neat polymers is usually observed, but the opposite effect is also reported in a number of cases. A number of proposals have been made to interpret this unpredictable behavior.

On one side the effective heat flux to which the polymer is exposed may not be constant, due to possible changes in the surface absorption/emission properties, for example as a consequence of surface charring. Other authors proposed, the origin on the thermal instability of layered clays organic modifiers, releasing fuel at relatively low temperature owing to the release of the excess of unbound organomodifier or by Hoffman decomposition, triggering polymer degradation by catalytic effects as well as viscosity increase hindering convective flow in the molten polymer. However, no solid experimental evidences are reported and no explanation is provided for the difference in ignition observed for similar polymer/nanoclay compounds.

The shorter ignition time has to correlate with some other change in material physical properties induced by the microparticles, leading to the earlier achievement of critical fuel production rate to reach the lower flammability limit. From bibliography the sample surface temperature profiles suggest that in nanocomposites, ignition may be controlled by nanoparticle-catalysed oxidation of the gases generated at the surface of the condensed phase by volatilisation of the polymer. Conditions for ignition are thus created as soon as the polymer decomposition temperature is reached, in contrast with pristine polymer in which enough volatiles from bulk polymer pyrolysis have to be produced to mix with air above the specimen to reach the lower flammability limit.

In summary, the results show that in general ignition times of the PVC foam nanocomposites are larger than that of pristine PVCK3 even though in some cases the amount of the additive (MWNT) in PVC is quite small. The increase on the ignition time would enhance fire retardant performance of Nanocore PVC foams.

A second parameter that is commonly used to evaluate the fire hazard of a material is the FIGRA index, an index originally used for the single burning item evaluation of fire spread that indicates the spread of fire, in our case the nanocomposites do not show a clear trend and it is difficult to appreciate any improvement when compared to pristine PVCK3 foam. In fact values are very similar to pristine PVCK3 foam or even worse (larger values), see PVCK3-MWNTs-5%.

Turning the attention to the FPI index, it clearly shows that addition of LDH modified with SDS lead to a slight increase on FPI compared to pristine PVCK3. FPI for PVCK3 with 5% of LDHSDS is 0.2 m²/s/kW some 40% higher than that of unmodified PVCK3 (0.12 m²/s/kW). A similar result is observed on the samples containing MWCNTS.

MWCNT-nanocomposite foam behavior can be explained because burning these materials a nanotubes network layer is formed which acts insulating the polymer-foam from the external radiant flux changing the transmission of heat from thermal conduction to radiative transfer. The nanotubes

layer becomes a physical shield decreasing external heat flux by one half and increasing also the ignition time with concentration.

Nanoclay-nanocomposite foams display a more erratic behavior, and their FST performance depends on both, nanoclay dispersion degree and modification type. In general, nanoclays protect the polymer by hindering the release of gases from inside the material, forming a barrier to degradation which helps to stabilize the outer layer.

It also important to highlight that in this case increasing LDH-SDP concentration up to 10% does not improve fire performance index but worsens it about 15%.

Samples with CNTs also perform better than pristine PVC3 and show a clear improvement with concentration, 20% better when compared to the original formulation due to a protective network formed at the surface.

In addition, to these reaction to fire tests, many transport applications are regarded as high risk ones in relation to fire safety. There is increasing concern about the generation of heat, smoke and toxic gases from polymers and composite components used in, for example, trains, ships and aircraft. European railway directives have recently been published concerning interoperability of trains across the EU and new fire classifications will be required for products installed in future European trains. NANOCORE foams have been tested following CEN45545 standard focus on evaluating smoke density and toxicity.

First results indicated that none of the NANOCORE samples release smoke at the same speed. PVCK3 foam (no nano additives added) shows the fastest smoke production rate, while PVCK3-LDH5% foam degrades 25% slower but reach the same density value (detector is saturated in less than 4 minutes).

The addition of CNTs completely changes the observed behaviour as the maximum density is not even reached within the test period (4 min) showing a reduction of 20% compared to PVCK3 foam. This result might be related to the physical shield created by the CNT network formed which hinder the smoke release. It can be deduced that the presence of MWNT does not decrease the quantity of polymer burned: but it slows considerably its combustion. During burning these structures are covered by a reflective black film which collapses at the end of combustion, forming the final structure of the residues.

Now, we turn our attention to the **toxicity of the effluents** by means of the CIT parameter. The failure criteria for CIT based on measurements of gas concentrations in the ISO 5659-2 test at 4 minutes and 8 minutes are specified in CEN 45545-2 in the range of 0.75 to 1.8 according to the family of products and to the required hazard level (HL) performance.

CIT value calculated according to CEN 45545 standard at 240 and 480s for all the NANOCORE foam samples tested in this work is below 0.75 which will indicate a toxicity fail for the HL category selected of the product.

Among the eight tracked components, CO and CO₂ are of great concern and more specifically CO because it is lethal at a relatively low concentration. It is worthy of remark, that at 4 min, *samples containing MWCTs release lower quantities of CO and CO₂, 21 and 31% respectively less than pristine PVCK3*. Similar trend is observed at 8 min with a reduction of 18 and 20% respectively with respect to neat PVCK3 foam.

In summary:

- **Nanocore Foams** compared to commercial ones show **higher ignition times making them safer in case of fire**
- On samples containing either LDH-SDP or MWCNTs, such as LDH-SDS-5 and MWCNT1-10, there is the largest diminution of fire spreads in a hypothetical fire.
- On samples containing MWCNTs, the greater the CNT content the larger the FPI index. The opposite behavior is observed on samples with LDH-SDP.
- The addition of CNTs completely changes the observed behaviour as the maximum smoke density is not even reached within the test period (4 min) showing a reduction of 20% compared to PVCK3 foam.
- According to CIT values, the smoke toxicity is really considerable and would not pass standards requirements for rolling stock as the maximum CIT value allowed is 1.8.

According to CEN 45545, the materials used in rolling-stock should be tested in the final configuration. In this case, Nanocore foams will be used to made GFRP sandwich panels, and were tested using two different skins. FR-Acrylic vs. polyester.

4. LIST OF DELIVERABLES

All deliverables listed in the technical annex of the Grant Agreement have been delivered on time or with very short delay, as shown below. Overall, 22 deliverables have been duly delivered to the EC. This is in addition to 2 internal reports presented in Table 2, and the quarterly management reports detailing the project progress status in every quarter during the project lifetime.

5. LIST OF MILESTONES

The NANOCORE milestones as specified in the technical annex of the Grant Agreement are presented below. All milestones were successfully met. Only milestone M4 is partially achieved, because due to the chemical composition of PVC foams and CEN45545 standard the material should be tested in the final configuration, it would means that tests should be carried out in the sandwich panel and not only in the NANOCORE foam. Once the test is done in the final configuration it fulfills all the requirements of CEN45545.

MS1: Workshop presenting knowledge in WP1 and technology developed in WP2-5
 Three most promising nanoparticle treatment methods and most promising nanoparticle and FR-additive combinations are selected.

MS2: Development of nanoclay surface treatment WP2
 Nanoparticles are dispersible in the polymer by melt-mixing without affecting the ability to mould the polymer and where nanocomposites agglomeration is reduced to less than 5%.

MS3: Nanoclay modification technology transfer
 Milestone is reached, when a pilot plant is producing the modified nanoparticles.

MS4: PVC based polymer with modified nanoparticles
 Results compliant with EN 45545 regulations and the viscosity of the new composite formulation does not exceed 10% of the viscosity of the pure PVC.

MS5: Workshop presenting to SMEs the knowledge and technical results obtained so far.
 Milestone achieved when workshop has been celebrated.

MS6: PVC based foam with modified nanoparticles
 a) Results compliant with EN 45545 regulations, b) results show an enhanced strength and stiffness at least 10% greater than the equivalent density of the unmodified foam.

MS7: FST results for sandwich panels using NANOCORE technology
 Sandwich panels based on NANOCORE technology fulfil FST regulations and mechanical specifications: 10% increase of stiffness as compared to existing PVC-panels.

MS8: Workshop presenting to SMEs the knowledge and technical results acquired by RTDs so far.
 Milestone achieved when workshop has been celebrated.

6. Use and dissemination of foreground

6.1. DISSEMINATION RESULTS (PUBLIC)

The NANOCORE project dedicated one work package (WP7) for the dissemination of the achieved results within the scientific and technical community. This WP7 is organized into six tasks, namely, Task 7.1: Review progress against scientific and technological objectives; Task 7.2: Review management of impact on economic and societal issues; Task 7.3: Workflow scheduling and work plan change control procedures; Task 7.4: Communication between partners within the work package; Task 7.5: Provision of the minutes taken at meetings and Task 7.6: Coordination of technical activities between partners within work packages.

Furthermore there is a specific WP dedicated to Innovation related activities, WP6, which focus on developing an Exploitation Strategy in the form of a plan that complies with the EC contract and the Consortium Agreement signed between the partners in order to protect the Intellectual Property Rights (IPR) arising from the technological developments in the project. These actions will be effective through a continuous patent search, contacts with global patent offices and definition of different protection possibilities for the planned results.

All these activities aim at ensuring absorption of the results by the participants and disseminate the knowledge developed during the course of the NANOCORE project and promote the exploitation of the results to the wider European Industrial Community.

The major dissemination results are summarized hereafter:

1.- Organization of workshops:

The project organized three events to transfer the knowledge generated by RTDS among the participating SMEs and two more events to disseminate and promote the project outcomes at two respective seminars gathering mainly the European experts from the industry and academia in the nautical field:

- 1^{er} Workshop presenting to SMEs the knowledge and technical results acquired by RTDs in Madrid, Spain, March 2012 (ACCIONA).
- 2^o Workshop presenting to SMEs the knowledge and technical results acquired by RTDs in Pisa, Italy, April 2013 (CGS).
- 3^o Workshop presenting to SMEs the knowledge and technical results acquired by RTDs in Zaragoza, Spain, June 2013 (ITA).
- Seminar to the Nautical industry in Pisa, (Navicelli Center), Italy, July 2013 (CGS).
- 4^o Workshop presenting to SMEs the knowledge and technical results acquired by RTDs in Pisa, Italy, July 2013 (CGS).

2.- Conferences and events:

Project outcomes have been disseminate by ITA, ACCIONA and Glonatech on international conferences.

- Participation to the workshop organized by Particoat Project “New Approaches to High Temperature Coatings” in Lanzarote, Spain, October 2012.
- Nanotech 2012, catedra SAMCA de nanotecnologia, in Zaragoza, Spain.
- Nanotech 2013, TechConnect, in Washington, USA, May 2013.
- EURONANOFORUM 2013, in Ireland, June 2013.
- MATCOMP 2013, in Algeciras, Spain, July 2013.
- TNT 2013, in Sevilla, Spain, September 2013.

Section A (public)

Publications

LIST OF SCIENTIFIC PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES											
No.	Title / DOI	Main author	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Date of publication	Relevant pages	Permanent identifiers (if applicable)	Is open access provided to this publication ?	Type
	Materiales Compuestos 13	Javier Sacristan Bermejo	Development of low FST hybrid composite		Asociacion Española de materiales Compuestos	Algeciras	02/07/2013	303		Yes	Conference

Template A2: List of all dissemination activities (publications, conferences, workshops, web sites/applications, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters).

LIST OF DISSEMINATION ACTIVITIES								
No.	Type of activities	Main Leader	Title	Date	Place	Type of audience	Size of audience	Countries addressed
1	Web sites/Applications	ACCIONA INFRAESTRUCTURAS S.A.	Project website	01/02/2012	www	Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias	10000000	all
2	Web sites/Applications	PLASTICOS KAREY SA	Wikipedia page describing NANOCORE	01/02/2012	http://en.wikipedia.org/wiki/Nanocore	Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias	10000000	all
3	Press releases	ACCIONA INFRAESTRUCTURAS S.A.	JEC2012	14/03/2012	JEC2012 Paris	Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias	1000	all
4	Exhibitions	ACCIONA INFRAESTRUCTURAS S.A.	JEC Europe 2012: the biggest composites exhibition in Europe and in the world	27/03/2012	Paris	Industry - Medias	29867	world wide
5	Organisation of Workshops	ACCIONA INFRAESTRUCTURAS S.A.	European Workshop New Approaches to High Temperature Coatings	15/10/2012	Lanzarote	Scientific community (higher education, Research)	50	Germany, Czech Republic, Italy, France, Spain, Russia, Greece
6	Flyers	ACCIONA INFRAESTRUCTURAS S.A.	NANOCORE	01/11/2012	Madrid	Scientific community (higher education, Research) - Industry - Medias		European countries
7	Organisation of Workshops	INSTITUTO TECNOLOGICO DE ARAGON	Meeting NANOTECH	18/12/2012	Zaragoza	Scientific community (higher education, Research) - Industry	50	Spain
8	Press releases	ACCIONA INFRAESTRUCTURAS S.A.	Development of foam core materials	09/04/2013	Cordis Wire	Scientific community (higher education, Research)	500000	all

						ion, Research) - Industry - Civil society - Medias		
9	Press releases	ACCIONA INFRAESTRUCTURAS S.A.	Making safer composite materials for ship building	10/04/2013	Cordis Press Corner	Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias	5000000	all
10	Press releases	ACCIONA INFRAESTRUCTURAS S.A.	Making safer composites for ship building	10/04/2013	http://hepinfo.net/node/132843	Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias	1000000	all
11	Press releases	ACCIONA INFRAESTRUCTURAS S.A.	Making safer composites materials for ship building	11/04/2013	http://phys.org/news/2013-04-safer-composite-materials-ship.html	Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias	10000000	all
12	Press releases	ACCIONA INFRAESTRUCTURAS S.A.	Making safer Composites for ship building	16/04/2013	http://www.safety4sea.com/page/15623/6/making-safer-composite-materials-for-ship-building	Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias	10000000	all
13	Oral presentation to a scientific event	Global Nanotechnologies S.A. for the Design, Development, Production and Trading of Nanotechnology Materials	DEVELOPMENT of a low FST and high mechanical performance hybrid nanocomposite material for ferries	13/05/2013	Whashington	Scientific community (higher education, Research) - Industry - Policy makers - Medias	5000	all
14	Organisation of Workshops	Global Nanotechnologies S.A. for the Design, Development, Production and Trading of Nanotechnology Materials	Participation in seminars undertaken by plastics industries in order to present NANOCORE project	12/05/2013	NYC, NY, USA	Scientific community (higher education, Research) - Industry - Medias	50000	all
15	Exhibitions	Global Nanotechnologies S.A. for the Design, Development, Production and Trading of Nanotechnology Materials	Organization of meetings with industrial organizations interested in thermoplastics composites and m	26/03/2013	NYC, NY, USA, Boston MA, USA	Industry	500	all
16	Videos	ACCIONA INFRAESTRUCTURAS S.A.	Nanocore's video-clip	07/06/2013	Madrid	Scientific community (higher educat	10000000	all

						ion, Research) - Medias		
17	Videos	ACCIONA INFRAESTRUCTURAS S.A.	Nanocore's video-clip has been uploaded to YouTube website	10/06/2013	http://www.youtube.com/watch?feature=player_detailpage&v=FM_W0RAy7wI	Scientific community (higher education, Research) - Industry - Civil society - Policy makers - Medias	10000000	all
18	Exhibitions	INSTITUTO TECNOLOGICO DE ARAGON	nano-tech based foams for enhanced mechanical performance and fire resistance in core materials for.	18/06/2013	Ireland	Scientific community (higher education, Research) - Industry - Policy makers - Medias	5000	all
19	Oral presentation to a scientific event	ACCIONA INFRAESTRUCTURAS S.A.	Development of low FST hybrid nanocomposite foam	02/07/2013	Algeciras, Spain	Scientific community (higher education, Research) - Industry - Medias	500	all
20	Organisation of Workshops	C.G.S. DI COLUCCIA MICHELE & C. S.A.S.	From the idea , to the project down to the funding	29/07/2013	Pisa, Italy	Industry - Policy makers	60	Italy
21	Organisation of Conference	C.G.S. DI COLUCCIA MICHELE & C. S.A.S.	Seminar to the nautical industry	29/07/2013	Navicelli Spa, Pisa, italy	Industry - Policy makers - Medias	100	Italy
22	Organisation of Workshops	C.G.S. DI COLUCCIA MICHELE & C. S.A.S.	Dissemination of NANOCORE main outcomes	02/10/2013	Genova, Italy	Industry - Civil society - Policy makers - Medias	500	all

Section B (Confidential² or public: confidential information to be marked clearly)

Part B2

OVERVIEW TABLE WITH EXPLOITABLE FOREGROUND								
Type of Exploitable Foreground	Description of Exploitable Foreground	Confidential	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application	Timetable for commercial use or any other use	Patents or other IPR exploitation (licences)	Owner and Other Beneficiary(s) involved
Commercial exploitation of R&D results	Chemical modification of nanoclays (LDH) with enhanced FST properties	No		Novel Fire retardant, and low smoke and toxicity additives.	Construction, transport, manufacturer of thermoplastic composites, masterbatches and blends	2014-2015	Filing a patent it's been considered by all partners	RTDs/SMEs
Commercial exploitation of R&D results	PVC nanocomposite foams with MWCTs with enhanced FST properties	No		Production of thermoplastic/MWCTs foams with very low smoke and toxicity production	transport	2015	Glonatech is considering filling a patent	RTDS/GLONATECH

ADDITIONAL TEMPLATE B2: OVERVIEW TABLE WITH EXPLOITABLE FOREGROUND	
Description of Exploitable Foreground	Explain of the Exploitable Foreground
Chemical modification of nanoclays (LDH) with enhanced FST properties	The purpose is to describe a novel type of organically modified layered double hydroxide with some selected surfactants containing phosphorous with enhanced FST properties.
PVC nanocomposite foams with MWCTs with enhanced FST properties	Developing of novel CNTs-based nanocomposites and nanocomposites foams with enhanced FST properties following the strictest EU standards.

² Note to be confused with the "EU CONFIDENTIAL" classification for some security research projects.

4.1 Report on societal implications

B. Ethics

1. Did your project undergo an Ethics Review (and/or Screening)?	No
If Yes: have you described the progress of compliance with the relevant Ethics Review/Screening Requirements in the frame of the periodic/final reports?	
2. Please indicate whether your project involved any of the following issues :	
RESEARCH ON HUMANS	
Did the project involve children?	No
Did the project involve patients?	No
Did the project involve persons not able to consent?	No
Did the project involve adult healthy volunteers?	No
Did the project involve Human genetic material?	No
Did the project involve Human biological samples?	No
Did the project involve Human data collection?	No
RESEARCH ON HUMAN EMBRYO/FOETUS	
Did the project involve Human Embryos?	No
Did the project involve Human Foetal Tissue / Cells?	No
Did the project involve Human Embryonic Stem Cells (hESCs)?	No
Did the project on human Embryonic Stem Cells involve cells in culture?	No
Did the project on human Embryonic Stem Cells involve the derivation of cells from Embryos?	No
PRIVACY	
Did the project involve processing of genetic information or personal data (eg. health, sexual lifestyle, ethnicity, political opinion, religious or philosophical conviction)?	No
Did the project involve tracking the location or observation of people?	No
RESEARCH ON ANIMALS	

Did the project involve research on animals?	No
Were those animals transgenic small laboratory animals?	No
Were those animals transgenic farm animals?	No
Were those animals cloned farm animals?	No
Were those animals non-human primates?	No
RESEARCH INVOLVING DEVELOPING COUNTRIES	
Did the project involve the use of local resources (genetic, animal, plant etc)?	No
Was the project of benefit to local community (capacity building, access to healthcare, education etc)?	No
DUAL USE	
Research having direct military use	No
Research having potential for terrorist abuse	No

C. Workforce Statistics

3. Workforce statistics for the project: Please indicate in the table below the number of people who worked on the project (on a headcount basis).

Type of Position	Number of Women	Number of Men
Scientific Coordinator	0	0
Work package leaders	0	0
Experienced researchers (i.e. PhD holders)	0	0
PhD student	0	0
Other	0	0

4. How many additional researchers (in companies and universities) were recruited specifically for this project?

0

Of which, indicate the number of men:

0

D. Gender Aspects

5. Did you carry out specific Gender Equality Actions under the project ?	Yes
6. Which of the following actions did you carry out and how effective were they?	
Design and implement an equal opportunity policy	Effective
Set targets to achieve a gender balance in the workforce	Almost effective
Organise conferences and workshops on gender	Not Applicable
Actions to improve work-life balance	Not Applicable
Other:	
7. Was there a gender dimension associated with the research content - i.e. wherever people were the focus of the research as, for example, consumers, users, patients or in trials, was the issue of gender considered and addressed?	No
If yes, please specify:	

E. Synergies with Science Education

8. Did your project involve working with students and/or school pupils (e.g. open days, participation in science festivals and events, prizes/competitions or joint projects)?	No
If yes, please specify:	
9. Did the project generate any science education material (e.g. kits, websites, explanatory booklets, DVDs)?	No
If yes, please specify:	

F. Interdisciplinarity

10. Which disciplines (see list below) are involved in your project?	
Main discipline	1.3 Chemical sciences (chemistry, other allied subjects)
Associated discipline:	1.2 Physical sciences (astronomy and space sciences, physics and other allied subjects)
Associated discipline:	2.3 Other engineering sciences (such as chemical, aeronautical and space, mechanical, metallurgical and materials engineering, and their specialised subdivisions; forest products; applied sciences such as geodesy, industrial chemistry, etc.; the

	science and technology of food production; specialised technologies of interdisciplinary fields, e.g. systems analysis, metallurgy, mining, textile technology and other applied subjects)
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G. Engaging with Civil society and policy makers

11a. Did your project engage with societal actors beyond the research community? (if 'No', go to Question 14)	Yes
11b. If yes, did you engage with citizens (citizens' panels / juries) or organised civil society (NGOs, patients' groups etc.)?	No
11c. In doing so, did your project involve actors whose role is mainly to organise the dialogue with citizens and organised civil society (e.g. professional mediator; communication company, science museums)?	
12. Did you engage with government / public bodies or policy makers (including international organisations)	Yes, in communicating /disseminating / using the results of the project
13a. Will the project generate outputs (expertise or scientific advice) which could be used by policy makers?	No

H. Use and dissemination

14. How many Articles were published/accepted for publication in peer-reviewed journals?	1
To how many of these is open access provided?	1
How many of these are published in open access journals?	1
How many of these are published in open repositories?	0
To how many of these is open access not provided?	0
Please check all applicable reasons for not providing open access:	
publisher's licensing agreement would not permit publishing in a repository	No
no suitable repository available	No
no suitable open access journal available	No
no funds available to publish in an open access journal	No
lack of time and resources	No
lack of information on open access	No

If other - please specify	
15. How many new patent applications ('priority filings') have been made? ("Technologically unique": multiple applications for the same invention in different jurisdictions should be counted as just one application of grant).	0
16. Indicate how many of the following Intellectual Property Rights were applied for (give number in each box).	
Trademark	0
Registered design	0
Other	0
17. How many spin-off companies were created / are planned as a direct result of the project?	0
Indicate the approximate number of additional jobs in these companies:	0
18. Please indicate whether your project has a potential impact on employment, in comparison with the situation before your project:	Difficult to estimate / not possible to quantify, In small and medium-sized enterprises
19. For your project partnership please estimate the employment effect resulting directly from your participation in Full Time Equivalent (FTE = one person working fulltime for a year) jobs:	0

I. Media and Communication to the general public

20. As part of the project, were any of the beneficiaries professionals in communication or media relations?	No
21. As part of the project, have any beneficiaries received professional media / communication training / advice to improve communication with the general public?	No
22. Which of the following have been used to communicate information about your project to the general public, or have resulted from your project?	
Press Release	Yes
Media briefing	No
TV coverage / report	No
Radio coverage / report	No
Brochures / posters / flyers	Yes
DVD /Film /Multimedia	Yes

Coverage in specialist press	Yes
Coverage in general (non-specialist) press	No
Coverage in national press	No
Coverage in international press	No
Website for the general public / internet	Yes
Event targeting general public (festival, conference, exhibition, science café)	Yes

23. In which languages are the information products for the general public produced?

Language of the coordinator	No
Other language(s)	No
English	Yes

Attachments	FINAL PUBLISHABLE SUMMARY REPORT.pdf, Nanocore video_MD.m4v, final_report_en_V3singrafs.pdf
Grant Agreement number:	262387
Project acronym:	NANOCORE
Project title:	Development of a low FST and high mechanical performance nanocomposite foam core material for ferries and cruise ship superstructures”
Funding Scheme:	FP7-BSG-SME
Project starting date:	01/09/2011
Project end date:	31/08/2013
Name of the scientific representative of the project's coordinator and organisation:	Mr. Antonio Sanchez Rojo ACCIONA INFRAESTRUCTURAS S.A.
Name	
Date	

This declaration was visaed electronically by María del Carmen MAESTRE (ECAS user name nmaestmn) on