The NANOFEU project : objectives and tools

Didier Calogine, Stéphane Duplantier, Carine Chivas, Eric Guillaume, José-Marie Lopez-Cuesta, Claire Longuet, Benoît Minisini, Francis Gensous, Loïc Chesne

The NANOFEU project: objectives and tools

Didier Calogine[1], Stephane Duplantier[1], Carine Chivas[2], Eric Guillaume[2], José-Marie Lopez-Cuesta[3], Claire Longuet[3], Benoit Minisini[4], Francis Gensous[5] and Loïc Chesné[5]

[1]INERIS, Parc Technologique ALATA, BP 2, 60550 Verneuil-en-Halatte, France

[2]LNE, CEMATE – Fire Behaviour Division, 78197 Trappe, France

[3]EMA, CMGD, 6 Avenue de Clavières, 30319 Ales, France

[4]ISMANS, 44 Avenue Bartholdi, 72000 Le Mans, France

[5]PlasticsEurope France, 14 rue de la République, 92800 Puteaux, France

E-mail: didier calogine@ineris.fr

Abstract. The NANOFEU project supported by the French Research Agency (ANR) aims to characterise the fire behaviour of nanoparticles filled polymer materials. Day after day, new applications of nanoparticles appear in industry. Among multiple applications in various domains, the role played by nanostructures particularly in combustion and flame retardancy phenomena needs to be quantified by modelling, experimental and numerical validations, since the use of these new components is increasing to upgrade polymer performances. Their employment could represent nowadays a valuable alternative or could be used in synergy with the conventional flame retardants systems. Nanocomposites based on several categories of polymers will be designed, incorporating suitable nanoparticles. Multiscale modelling of material, investigation of thermal degradation processes, and influence of interfacial modifications of nanoparticles, characterisation of effluents, particles released (size and morphology) and smoke toxicity will be made, developing original experimental and numerical means. We will particularly focus on fire performance, smoke toxicity and morphological modification of particles in the effluents, to weight the various impacts of the introduction of these nanofillers. A traceability of nanoparticles affected by combustion will be done through the analysis of effluents. In a first part, this paper includes a detailed presentation of the project by clarifying the partners' roles and objectives expected at the end of the project. In a second part, the foreseen experimental and numerical tools will be developed in order to improve the knowledge of mechanisms involved in combustion.

1. Introduction

Nanoparticles have changed the perception of the concept of polymer composite. Nanocomposites are the emerging material of the 21st century. The importance of these products is growing from industrial and research point of view. These materials represent with their complexity new economical, scientific, technical and social challenges. Estimated at 40 billion Euros in 2001, the world market of nanotechnologies would exceed the 1000 billion Euros in the next ten years.

Nanocomposites have been observed to exhibit enhanced mechanical properties [1]. They represent a combination of unique properties, such as increased heat resistance temperature, reduced permeability, reduced flammability and improved mechanical properties. As for any new development, advantages and drawbacks of these new products must be precisely evaluated.

It is useful to have resistant materials in domains pertaining to buildings and to transport in case of fire. To reduce the flame propagation, some fire-retardants systems usually employed cannot satisfy the environmental requirements.

The non-halogenated flame resistant systems represent consequently a way of substitution but to reach the aimed performances, a strong mass percentage is necessary. Consequently another way lies in using nanoparticles with appropriate properties. It consists in developing systems containing particles allowing to modify the thermal degradation or the inflammation of polymer materials. The association of organo-modified nanoparticles or those treated on surface with polymers modified by the incorporation of specific monomers, as well as with additive flame retardants non-halogenated, aimed at obtaining high levels of protection against fire.

In this context, the NANOFEU project aims to get performances in terms of fireproofing of nanocomposites while analyzing the released products in terms of gaseous effluent.

2. Description of the project

The primal reason for incorporating fire retardants into these materials is to reduce hazard due to fire. Fire retardants strategies aim to reduce the ignitability or the rate of heat release of burning material but the results produce toxic gas and smoke responsible to several deaths [2].

Polymer nanocomposites offer a wide range of promising applications because of their enhanced properties arising from the reinforcement using nanoparticles. They are often reinforced by stiff fillers to improve mechanical properties. The efficiency of this reinforcement depends on the filler aspect ratio, the filler mechanical properties and the adhesion between the matrix and the filler. It is expected that their presence within the fireproofed composite improved effects barriers in developing a synergy between the various actors within the matrix. Further development depends on the fundamental understanding of the hierarchical structures and behaviours which requires multiscale modelling and simulation strategies to provide the coupling of various time scales and length scales [3]. According to the physical scale studied, a hierarchy of models can be applied using various numerical tools from molecular dynamics simulation to macroscale models. At mesoscopic scale studies initiated by Nielsen [4] allows to set up laws taking into account physical properties of both matrix and inclusions.

The NANOFEU project, started in January, 2008 for 3 years, is a research program carried out in collaboration between five complementary partners: “Institut national de l’environnement industriel et des risques” (INERIS), “Laboratoire national de métrologie et d’essais” (LNE), “Ecole des Mines d’Alès” (EMA), “Institut Supérieur des Matériaux et Mécaniques Avancés” (ISMANS) and Plastics Europe France. All the partners will share their knowledge in combustion, polymers and nanoparticles fields in this joint project.

2.1. Presentation of partners

Under the supervision of the French Ministry for Environment, Energy, Sustainable Development and Land settlement, INERIS coordinator of this project, assesses the processes, the techniques of prevention and potential effects of accidents or pollutions. This institute evaluates the risks pertaining to the development of new technologies.

The LNE, connected with the Ministry-delegate for Industry, has for missions the certification of products and the global piloting of the French metrology. This laboratory has specific devices for the characterization of the materials behaviour in fire.

Placed under the technical supervision of the Ministry-delegate for Industry, EMA developed its skills in the field of the Sciences of materials and in particular in the study of high diffusion materials (polymers, asphalts, concretes) and the interfaces from microscopic to macroscopic scales.

ISMANS brings to this project his assessment in numerical design of materials and functional devices and also in virtual engineering and non linear mechanics. This partner is charged of the modelling and the molecular simulation of nanocomposites behaviour in fire.

Plastics Europe France represents the French analogue of the European syndicate of the plastics producers. It includes the various companies working in the domain such as ARKEMA, SOLVAY, LVM.

2.2. Objectives

The aim of this project is to acquire knowledge on the efficiency obtained by the addition of nanostructure within polymer and to define the toxicity inherent to the development of nanocomposites [5].

For that, comparisons are elaborated with regard to properties and behaviours of polymer with various additives such as nanoparticles, modified nanoparticles, flame retardants and combinations of nanoparticles and IFR.

Objective consists in studying new concepts of fireproofing such as effects barriers and in developing effects of synergy particularly by combining aspects of nanoparticles and intumescences.

Flammability and fire toxicity depend on scenario and type of sample. That is why several shapes will be treated. Bench-scale determination of toxic product yields in fire effluents will be produced associated to particular methodologies.

The flame-retardants efficiency of samples will be improved by simultaneous test analysis to define the thermal degradation characteristics of products. Indeed nanoparticles have an influence on the thermal stability of polymers according to two mechanisms: by barrier effect in volatilization gases or combustive and by local modification of the polymer morphology (creation of an interphasis between matrix and nanofiller).

Relations between structures and properties at various scales will be studied by leaning on methodological steps and experimental approaches [6]. For that, the dynamic molecular tool at nanoscopic scale using specific potential of correlation will be investigate to obtain thermal properties of samples such thermal conductivity and resistivity of microscopic structure. Methods of validation such as simulation by flash method can complete this procedure for the determination of sample physical properties.

This project proposed to improve one's knowledge of the role played by nanostructure in the polymer matrix. Procedure is summed up in two stages:

1. Use of experimental methods for the measure of thermo physical parameters
2. Study, modelling and simulation of nanocomposites combustion.

3. Materials and methods

A number of experimental and numerical procedures will be used in the framework of this project:

3.1. Preparation of the nanocomposites

Nanocomposites can be synthesized by different routes. Most commonly used processes are realized using melt-intercalation, in-situ polymerization, solution and emulsion polymerization.

Samples used in this project will be made by EMA by melt mixing of the components.

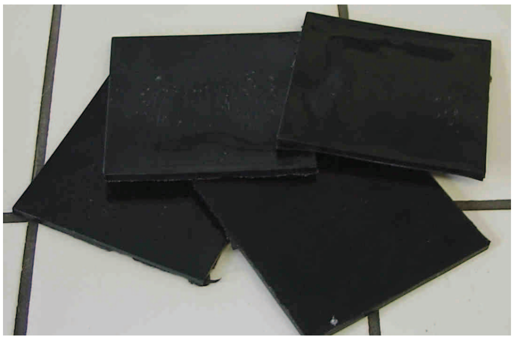


Figure 1. Kind of elaborated samples

3.2. Experimental techniques used to characterize the sample

Studies show that, concerning the toxicity of nanoparticles, effects at medium and long term depend on size and on form of particles. That is why analysis of samples is primordial. Studies of structural and morphological characteristics were carried out.

Various techniques will be used, such as Transmission Electron Microscopy (TEM) to observe the uniformity of dispersion in the polymer matrix, Thermogravimetry Analysis (TGA) to determine the influence of nanofillers on the thermal comportment of composite, Scanning Mobility Particle Sizer for the determination of size distribution of particle …

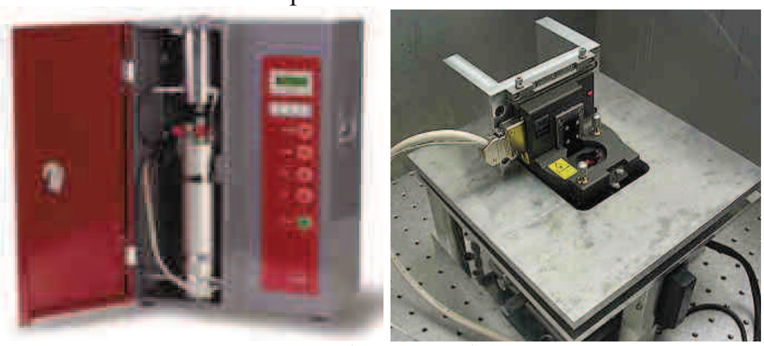


Figure 2. ELPI impactor and AFM spectrometer

3.3. Combustibility characteristics

On one hand, the flammability properties of samples with different percentages of fillers will be measured by fire calorimeter. The fire calorimeter is a commonly used device to measure the mass loss rate per unit area and the heat release per unit area for a given constant external radiative heat flux. Chemical energy release date, mass loss rate and time of ignition will be evaluated. Ignitability and flammability tests will be performed according to standard procedures.

On the other hand identification and quantification of combustion gases and particularly their toxic components from different fire scenarios were undertaken by continuous Fourier Transform Infrared spectroscopy (FTIR). The spectra of the decomposition and combustion products of various materials will be collected.

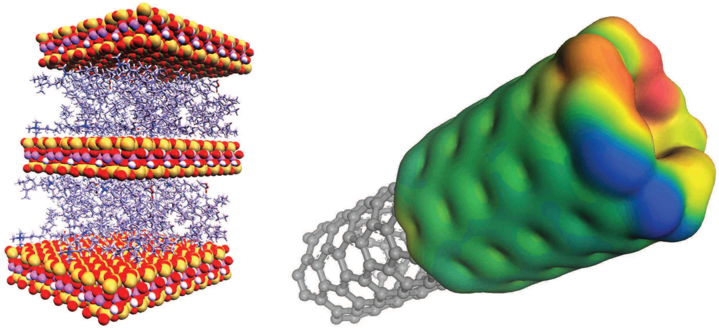
Figure 3. Teawarson calorimeter and TFIR metrology

3.4. Numerical tools

In the last decade molecular modelling tools were extensively used to study the properties of nanocomposites systems at different scales. For example, Density Functional Theory (DFT) was used to evaluate the mechanical or electrical properties of nanotubes whereas Molecular Dynamics (MD) was used to have a molecular insight into the interactions between polymers and nanoparticles.

On other hand, it appears from experimental studies that the chemical reactivity of polymer in presence of nanocharges is different too in the bulk. Consequently, some questions arise on radical stability, new reaction pathways catalysed by nanoparticles and so on. Moreover, the presence of combustion products can play a role in the aggregation of the nanoparticles and consequently affect the size and the morphology of particles released.

In this project, a methodology will be developed to assess the role of nanoparticles in the thermal degradation of polymer resin. DFT, MD and hybrid methods associated with atomistic models will be used for this purpose.



Figures 4. Examples of dynamic molecular simulations

References

[1] Valavala P K and Odegard G M 2005 *Rev. Adv. Mater. Sci.* **9** 34
[2] Stec A A, Hull T R, Purser J A and Purser D A 2008 *Fire Safety Journal* **44(1)** 62
[3] Zeng Q H, Yu A B and Lu G Q 2008 *Prog. Polym. Sci.* **33**, 191
[4] Nielsen L E 1967 *J. Macromol. Sci. Chem*. **5(1)** 929
[5] Chivas C, Guillaume E, Saragoza L, Ducourtieux S, Sainrat A and Macé T 2008 Biannual Conference on modification, degradation and stabilisation of polymers, Belgium
[6] Picken S J, Vlasveld D P N, Bersee H E N, Ozdilek C and Mendes E 2008 "Structure and mechanical properties of nanocomposites with Rod- and Plate-Shape nanoparticles" in Nanocomposites: Ionic conducting materials and structural spectroscopies, P. Knauth and J. Schoonman (eds.)