

Properties of Nanofillers in Polymer

Damien M. Marquis, Éric Guillaume* and Carine Chivas-Joly
Laboratoire national de métrologie et d'essais (LNE)
France

1. Introduction

Polymer nanocomposites have existed for decades, as carbon black, pyrogenic silica and diatomite were used as additives in polymers. Nevertheless, their characterizations and the effect of properties induced by the nanometric scale of fillers was not fully understood at these times. The real starting point, corresponding to an understanding of the action of these fillers, is generally considered as corresponding to the first papers on a polyamide-6 filled with nanoclays published by Usuki et al. (1993) and Okada A. (1995), from Toyota R&D. Both these papers called it "Hybrid" material. Rapidly, research increased, and the first use of the term "nanocomposites" appeared in 1994 [Lan & Pinnavaia (1994), Lan et al. (1995), Giannelis (1996)]. After these pioneers, a lot of researches started on various fillers. The demand for continual improvement in the performances of thermoplastic and thermoset polymer materials has led to the emergence of these new technologies. Nanofillers lists increased within years (nanoclays, nano-oxides, carbon nanotubes, POSS, etc.), as well as the matrix in which they are used and interactions with traditional fillers. Nowadays, the development of polymer nanocomposites is one of the most active area of development of nanomaterials. The properties imparted by the nanoparticles are various and focus particularly on strengthening the electrical conduction and barrier properties to temperature, gases and liquids as well as the possible improvement of fire behaviour. As a method which consists of reinforcing polymer chains at the molecular scale in the same way than the fibres at the macroscopic scale, nanocomposites [Biron (2004), Gloaguen & Lefevre (2007)] represent the new generation of two-phased materials, associating a basic matrix to nanofillers inserted between polymer chains. Nanofillers can significantly improve or adjust the different properties of the materials into which they are incorporated, such as optical, electrical, mechanical, thermal properties or fire-retardant properties, sometimes in synergy with conventional fillers. The properties of composite materials can be significantly impacted by the mixture ratio between the organic matrix and the nanofillers.

2. Classification of nanocomposites

2.1 Terminology

Terminology issues were solved recently with standardization. A standardization committee, ISO TC229 "Nanotechnologies", started in 2005, and a joint working group with IEC 113 "Nanotechnology Standardization for Electrical and Electronic Products and Systems" considered terminology and nomenclature issues. This group produced a set of documents

*Corresponding author

limiting confusion in definition of nano-objects [ISO/TS27687 (2008), ISO/TS11360 (2010), ISO/TS88004 (2011)].

Nanocomposites are considered as one family of nanomaterials, where a nano-object is

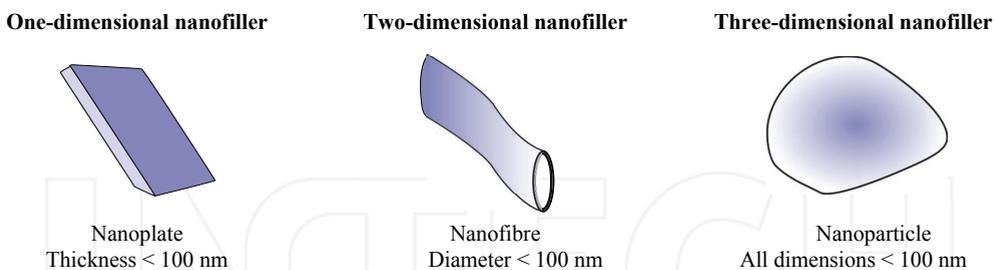


Fig. 1. Nano-objects used for nanocomposites, as defined in ISO/TS27687 (2008)

dispersed into a matrix or a phase. The other families are mainly nanostructured materials in surface, multi-layer or volume. A nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nm [Ajayan et al. (2003)]. The nanocomposites can be distributed according to the nanofillers, as classified in reference [ISO/TS27687 (2008)] and highlighted in Fig. 1:

- One-dimensional nanofiller: in the form of plates, laminas and/or shells;
- Two-dimensional nanofiller: nanotubes and nanofibres which diameter is lower than 0.1 μm ;
- Three-dimensional nanofiller: isodimensional nanoparticles such as nanometric silica beads.

Nanofillers are introduced in polymer at rates from 1% to 10% (in mass). They are incorporated in addition to traditional fillers and additives, and eventually traditional reinforcement fibres such as glass, carbon or aramide fibres. The diverse nanofillers used are described in the following paragraphs.

2.2 Nanoclays

Nanoplate fillers can be natural or synthetic clays, as well as phosphates of transition metals. The most widely used reinforcement is clay due to its natural abundance and its very high form factor. Clay-based nanocomposites generate an overall improvement in physical performances. The most widely used ones are the phyllosilicates (smectites). They have a shell-shaped crystalline structure with nanometric thickness. Clays are classified according to their crystalline structures and also to the quantity and position of the ions within the elementary mesh. The elementary or primitive mesh is the simplest atomic geometric pattern, which is enough for duplicating the crystalline network, by repeating itself indefinitely in the three directions. Table 1 presents the various natural and synthetic nanoclays available and used as fillers in polymers. The most common usage concerns organomodified Montmorillonite (MMT), a natural phyllosilicate extracted from Bentonite. Raw formula of Montmorillonite is $(\text{Na}, \text{Ca})_{0,3}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2, n\text{H}_2\text{O}$.

2.3 Nano-oxides

Titanium dioxide: Rutile is commonly used in polymers as a white pigment, as particles from 200 to 300 nm. The nanoparticle of titanium dioxide is not Rutile, but Anastase, and both are

Family		Groupe	Formula
Phyllosilicates	TO(1:1)	Kaolinite	The reference plate is formed from a tetrahedral plate T and a octahedral plate O. The thickness of the layer is about 0,7 nm. Kaolinite $Al_4 Si_4 O_{10} \cdot (OH)_8$
	TOT(2:1)	Smectite, (Talc, Mica, Mommorillonite), Sepiolite	Two tetrahedral plates T in both sides of an octahedral plate O form the reference plate. The thickness of the layer is about 1 nm. The group includes many minerals that are major constituents of clays.
	TOT:O(2:1:1)	Chlorite, Bentonite, Saponite	The reference plate is formed of three plates TOT and another isolated O plate. The thickness of the layer is about 1,4 nm. Chlorite di-tri $Al_2 Mg_3 Si_4 O_{10} (OH)_8$
Polysilicate	Natural	Kenyaite, Magadiite, Kanemite, Illerite, Silhydrite, Zeolite.	Magadiite ($Na_2 Si_{14} O_{29} H_2 O$)
	Synthetic	FluoroHectorite, Zeolite	
Double lamellar hydroxide	Synthetic	Hydrotalcite	Hydrotalcites: $(Mg_6 Al_2 (OH)_{16}) (CO_3^{2-})_4 H_2 O$

Table 1. Nanoclays identification.

tetragonal crystal forms of titanium dioxide. Anatase is commonly used as spherical particles with diameter around 20 nm. This nanoparticle has photocatalytic properties. Anatase can be converted by hydrothermal synthesis into titanium nanotubes [Mogilevsky et al. (2008)]. These nanotubes have an outer diameter of 10 to 20 nm, an inner diameter of 5 to 8 nm and a length of 1 μm . *Nanoalumina*: Alumina particles are used as fillers in a wide range of size, from 20 nm to micrometric sizes. They are made of spherical crystal particles of $Al_2 O_3$. Nanoparticles of alumina are frequently used as inert fillers in polymers, but highlight catalytic properties in some conditions. *Nano-antimony-Tin oxide (ATO)*: The raw formula of this nanoparticle is $Sb_2 O_5 / SnO_2$. This is a tetragonal crystal particle of a diameter of around 15 nm, commonly used as flame retardant. *Nanosilica*: Nanosilica correspond to a large family of nanoparticles from various origins. The most commonly used is a natural one, called diatomite. This filler comes from the skeleton of a unicellular algae (the diatomea) forming sedimentary layers. It is constituted from ultrafine particles of 750 nm. Two families of widely used synthetic nanosilicas are pyrogenic silica, forming particles from 5 to 100 nm, and silica fume, forming particles of about 100 nm. Precipitated silica historically used in polymers is not a nanoparticle, as its diameter is between 1 and 10 μm when micronized.

2.4 Carbon nanotubes

Carbon nanotubes (CNT) were discovered by [Oberlin et al. (1976), Endo et al. (1976)], without application, and then rediscovered by [Iijima (1991)]. The fibre could present a nanometric diameter and length of some orders of magnitude in comparison with its diameter. In general, three kinds of carbon nanotubes are considered (Fig. 2):

- Single-wall carbon nanotubes (SWCNT). They present a diameter between 1 and 2 nm;

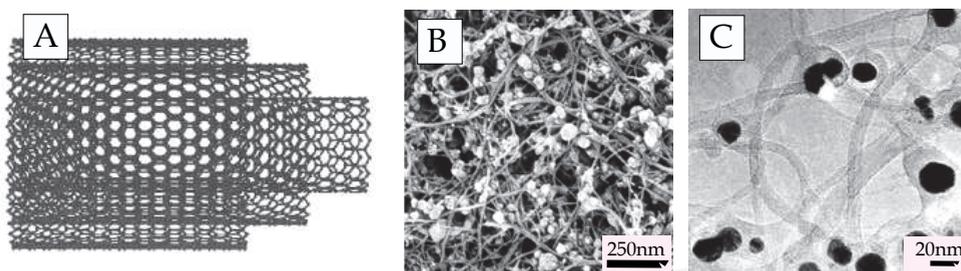


Fig. 2. Carbon nanotubes. a) Multi-Wall carbon nanotube (MWCNT). Idealized view; b) SEM image of nanotubes obtained by arc with 30 to 40 wt% catalytic residues (width of picture corresponds to 2 μm); c) TEM image showing the catalytic residues within nanotubes with 25 wt% catalyst residue.

- Double-wall carbon nanotubes (DWCNT). Diameter is between 2 and 4 nm;
- Multi-wall carbon nanotubes (MWCNT). They present a diameter between 4 and 150 nm.

These nanotubes present a theoretical range of properties incredible (Young modulus up to 1 TPa, heat conductivity of 3000 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, electric conductivity of 107 $\text{S}\cdot\text{m}^{-1}$, etc.), but considering perfect nanotubes individually makes no sense. They nevertheless provide a wide range of new properties when used in nanocomposites, depending on their purity and dispersion in the matrix.

Carbon nanotubes are produced by two possible ways: a catalytic chemical vapour decomposition process at medium temperatures (600-1000°C) and an electric discharge (arc) process under helium at high temperature (3000 to 4000°C). Both processes produce a mix between SWCNT, DWCNT and MWCNT, with surface defaults (e.g. some pentagonal cycles in place of aromatic rings), and present important catalytic residues. Another important parameter is the chirality of the CNT (i.e. the direction and deviation in the "roll" process of CNT), only when they are studied individually, as the processes generate a mix of all possible chiralities.

2.5 Other nanofillers

Metallic nanoparticles: Most common metallic nanoparticles are nanosilver, nanozinc and nanogold fillers. These particles have a catalytic behaviour, which leads to antibacterial properties at surface. Their electrical and magnetic properties are also used for nanocomposites. **Silsesquioxanes:** Silsesquioxanes are big synthetic cage macromolecules used as nanofillers in polymers. Their raw formula has been found to be $R - \text{SiO}_{3/2}$ with R typically being alkyl or organo-functional groups. The high three-dimensional symmetry and nanometer size make silsesquioxanes building blocks for nanocomposites. The diversity of possible functional groups along with their controlled orientation in 3-D space allows for highly tailored nanometer-by-nanometer construction in all three dimensions. An example of a silsesquioxane structure is given in Fig. 3.a). The most common Silsesquioxanes found are polyhedral oligosilsesquioxanes (POSS), octasilsesquioxanes of the $[\text{ROSiO}_{1.5}]_8$ type and its polymeric derivatives, and $[\text{R} - \text{phenylSiO}_{1.5}]_8$ type and its polymeric derivatives. They are used to make structured 3-D nanocomposites for thin films, monoliths, and fibre reinforced composites. At present time, their expensive price limits their usage in polymers. **Boehmite:** Boehmite is a mineral aluminium hydroxide orthorhombic dipyramidal cristal used as a

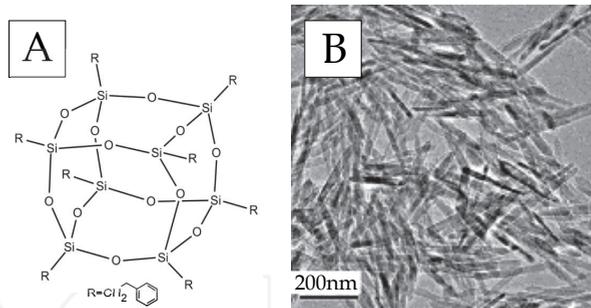


Fig. 3. a) Silsesquioxanes ; b) Boehmites.

nanofiller in nanocomposites. It could be obtained naturally or from chemical synthesis from saturated solutions. Its raw formula is $\gamma - AlO(OH)$. A picture of boehmite nanorods is given in Fig. 3.b.

3. Production of nanocomposites

3.1 Functionalization and dispersion of the nanofiller

As stated previously, two of the governing parameters for the properties of nanocomposites are the dispersion of the filler and its interaction with the matrix. Both are influenced by the usage of a chemical treatment at the surface of the filler. This surface treatment is possible for every kind of nanofillers. The use of nanofillers in thermoplastics and thermoset resins [Suh et al. (2000)] requires pre-treatment to improve the interfacial interactions between the filler and the matrix. The introduction of appropriate organic links between the matrix and the filler by functionalization improves the intercalation of polymer chains between the layers.

3.1.1 Nanoclays

MMT is extracted from the bentonite by a process of sedimentation in water [Kornmann et al. (1998)], and then activated by sodium ions (Na^+) to improve clays swelling. It is then possible to insert organic cations, such as silanes [Fu & Qutubuddin (2004)], ammonium bromides [Kornmann et al. (1998)] or ammonium chlorides such as vinylbenzyl octadecyldimethyl ammonium chloride (VOAC) or vinylbenzyl dodecyldimethyl ammonium chloride (VDAC) [Chen et al. (2007a)]. These ions reduce the surface energy of clay, making it more organophilic, thus facilitating access between the layers of monomers and polymers with different polarities. Nowadays, pre-modified MMT are often used and commercially available (Cloisite[®], Garamite[®], etc). The incorporation of montmorillonite-layered silicates in a thermoplastic melt needs the exchangeable cations or alkaline earth from the clay to be replaced by organophilic cations. The organophilic cations used are commonly quaternary ammoniums. Fig. 4.a presents commonly used cation for polyethylene and propylene nanocomposites. Fig. 4.b presents commonly used cation for polyamide nanocomposites. The apophyllite (Phyllosilicate of formula $KFCa_4 [Si_8O_{20}], 8H_2O$) can be functionalized by silylation reaction [Dean et al. (2007)]. The apophyllite functionalized (*n*-Octylsiloxy apophyllite) can be introduced into polyester or vinyl ester resins. Dean et al. (2007) studied the influence of the implementation of nanoclay composite/epoxy on the improvement of composite properties, using various dispersal methods (mechanical or ultrasonic methods) and various concentrations of nanoclay (mass fraction 0, 1, 2.5 and 5%). The author

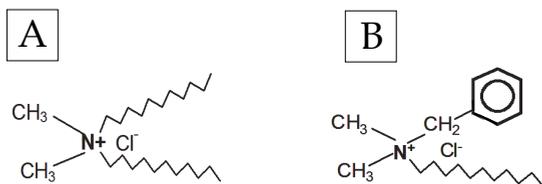


Fig. 4. Example of quaternary ammonium used for exfoliation in thermoplastics nanocomposite production. a) Nanowire 5; b) Nanowire 9

highlighted a strong influence of this parameter. The objective is to obtain an interaction between the nanofiller and the matrix at the nanometric scale. The intercalated structure is the common objective when dealing with nanoclays, as shown in Fig. 5 for example. Three



Fig. 5. Dispersion of modified nanoclay into poly ϵ -caprolactone (PCL), from Labidi et al. (2010). Width of the picture is 250 nm

cases are possible, which affect considerably the properties of the material:

1. The nanofillers are not mixed with the matrix, but form regions. The material is then a microcomposite.
2. The polymer matrix intercalates into the filler, between plates.
3. The fillers are totally exfoliated and dispersed

3.1.2 Nano-oxides

The use of metal oxides as nanofillers requires surface functionalization of these nanoparticles. Guo et al. (2007) and Guo et al. (2008) have reported the functionalization of Fe_2O_3 and other oxides by methacryloxypropyl trimethoxysilane di-functional in tetrahydrofuran. The objective with nano-oxides is to obtain a maximized exfoliation and full dispersion into the matrix.

3.1.3 Carbon nanotubes

The objective of carbon nanotubes is to maximize the dispersion into the matrix. The dispersion of CNTs in a thermoset matrix type can be improved without modifying the surface of CNTs and thanks to high shear rates [Song & Youn (2005)]. The dispersion can also be improved by functionalizing the surface of CNTs. These modifications improve the interfacial interactions with the matrix. Three ways are possible:

3.1.3.1 Chemical functionalization (covalent bounds):

Various techniques exist for the chemical functionalization of carbon nanotubes:

- Functionalization by exposure to ultraviolet rays and ozone [Sham & Kim (2006), Li et al. (2008)] to introduce carboxylic acid groups on the surface. This UV/O_3 treatment improves the dispersion and interfacial adhesion of CNTs to the epoxy matrix.
- Functionalization with amines [Fiedler et al. (2006), Shen et al. (2007), Chen et al. (2008)]: The amine can form covalent bonds with the epoxy matrix. The first reaction requires the formation of carboxylic acid binding on the nanotube. This carboxylation can be carried out by adding an acid (H_2SO_4/HNO_3) [Shen et al. (2007)] or amino dendrimers (APNM-O) [Sun et al. (46)].
- Functionalization with silanes [Ma et al. (2007)]: CNTs are first oxidized by exposure to UV in the presence of ozone, then reduced in a hybrid aluminum-lithium solution followed by a silanization. This functionalization with silanes improves the dispersion of CNTs in matrix just like epoxy improves thermal and mechanical properties but decreases thermal conductivity.
- Functionalization of bridges by adding poly(acryloyl chloride) (PACl) [Zou et al. (2008)]: PACl functionalized CNT react with epoxy monomers. CNTs thus grafted epoxy (epoxy-CNT) are mixed with an epoxy resin. This technique improves the thermal and mechanical properties while working at very low rates of CNT (0.1-1.0 wt%).
- Functionalization by an epoxy group [Chen et al. (2006)]. Multiwall CNT (MWCNT) are functionalized monomer diglycidylether of bisphenol A (DGEBA). The monomer is then added to the functionalized MWCNT and the addition of a tertiary amine results in the anionic polymerization of this monomer and the creation of covalent bonds between the resin matrix and the MWCNT-epoxy.

3.1.3.2 Physical functionalization:

The dispersion of CNTs in a thermoset matrix can be improved by non-covalent physical treatments, which have the advantage of not damaging the structure of the CNT, or introduce defects.

- Functionalization by adding a surfactant [Fiedler et al. (2006), Fan et al. (2004), Geng et al. (2008)]: physical adsorption of surfactant on the surface of CNTs decreases its surface tension, which prevents the formation of aggregates. Polyoxyethylene octyl phenyl ether (or Triton X – 100®) is frequently used as a non-ionic surfactant for MWCNT. The hydrophobic part of the surfactant is absorbed by the CNT, while the hydrophilic part forms hydrogen bonds with the matrix.
- Functionalization by metal ions: The functionalization of CNTs could be performed with Ag^+ by a mixing process in the presence of ammonium bicarbonate [Ma et al. (2007), Zhao et al. (2008b)]. It could also be done coating CNTs with nickel [Zhao et al. (2008b)], silver nanowire [Zhao et al. (2008a)] or iron [Zhao et al. (2009)] encapsulated inside the nanotube.

3.1.3.3 Surface deposition:

The dispersion can also be improved by plasma deposition of a very thin polymer film (2-7 nm) on the inner and outer surfaces of CNTs [Shi et al. (2003), Lee et al. (2007)]. The dispersant may also be a block copolymer [Cho et al. (2008)].

3.2 Processes of nanocomposite production

3.2.1 Nanoclays and nano-oxides

For nanoclay-based composites, three main ways are used for the synthesis of nanocomposite:

- In-situ: monomer is introduced between clay plates, then polymerized in-situ.
- Direct: polymerization and incorporation into clay plates are performed together simultaneously. It could be performed using temperature as the initiator for thermoplastics, or by catalyze during the polymerization process (solution-assisted)
- Co-precipitation: clays and precursors are dispersed together in a solution, then co-precipitated by a catalytic way.

The important aspect to control during the process is then the homogeneity of the dispersion. If nanoparticles are aggregated inside the material, it could lead to the formation of a microcomposite and nanoscale interactions could not be obtained. A large majority of authors working at laboratory scale with nanocomposites (especially thermosets) use the same manufacturing process based on the direct way, described by the company Ashland [Twardowska & Dammann (2005), Twardowska et al. (2005)] as follows:

1. Chains of polymer (commonly polyesters or vinylesters) are mixed with styrene and nanofillers previously treated and functionalized (in order to improve exfoliation).
2. The mixture is mechanically stirred at a high shear rate to improve the intercalation, and then placed under vacuum to remove air bubbles. To improve the dispersion of the filler in the resin, a step of cold ultrasound sonication is used.
3. At room temperature, an initiator (methyl ethyl ketone peroxide, MEKP) and an accelerator (cobalt-octate) are added for the crosslinking step. The high viscosity mixture is mixed, then again placed under vacuum to remove air bubbles before being poured into a mold previously covered with a coating limiting the membership of the mixture (paraffin and polyvinyl acetate, Teflon). The mold is rotated so as to avoid sedimentation of particles in the bottom of the mold. Crosslinking is obtained through successive stages of cooking and post-baking pan (called "cure" and "post treatment").

Some variations could also be found in the relevant literature [Suh et al. (2000)]. Patent [Nichols & Chou (1999)] concerning a large number of resins and inorganic materials in the form of plates mention also a classical in-situ polymerization method.

3.2.2 Carbon nanotubes

Nanocomposites containing carbon nanotubes are made by different processes, depending on whether or not prepreg (fibre mat) is used. The various nanocomposites that do not use pre-impregnated fibre processes are high-speed mechanical stirring [Xu et al. (2004)] and 3-roll milling process [Seyhan et al. (2007a), Seyhan et al. (2007b)]. Nevertheless, one of the main applications for nanocomposites containing carbon nanotubes is the casting of a large object subjected to high stresses. These materials often contain glass or carbon fibres reinforcing type and layout requires special techniques such as Wet/Hand lay-up process [Chandradass et al. (2007)], Resin Transfer Molding (RTM)[Schubel P.J. (2006), Wichmann et al. (2006), Fan et al. (2004)], or Vacuum Assisted Resin Transfer Molding (VARTM) [Hsiao & Gangireddy (2008), Sadeghian et al. (2006), Zhu et al. (2007)].

Layered hybrid materials (laminates) in thermoset matrix containing carbon nanotubes and reinforcing glass fibres are manufactured in 2 stages: CNTs are separated and dispersed in the mixture containing the polymer (by 3-roll milling process or ultrasound). In a second step, the

suspension polymer / CNT is added to a mat of fibre (prepreg). Processes referred previously could then be used. Depending on the matrix, viscosity of the mix and process used, the incorporation of CNTs could be performed up to 2% in mass.

4. Properties of nanocomposites

4.1 Modification of mechanical properties of thermoset composites

4.1.1 Nanoclays

Application to resin concrete: Nanoclay, treated and untreated montmorillonite were incorporated to strengthen a resin concrete (11% polyester resin and 89% of mineral fillers (sand and limestone)) [Jo et al. (2008)]. Only the treated montmorillonite increases the strength and modulus in compression of concrete. An increase of 20% of the mechanical properties is obtained for a rate of nanofillers between 5 and 7%. Without surface treatment, performances are comparable to those lacking of nanofiller. Exfoliation is supposed to explain the differences.

Application to polyester resins: [Bauer et al. (2008)] shows that the strengthening of a polyester resin by montmorillonite nanofillers treated by grafting silane functions led to a sharp increase in mechanical properties and in particular the energy propagation of rupture. Value is doubled compared to the virgin resin, with a proportion of nanofillers 1.5% by volume. The mixing time between treated montmorillonite and hydroxypropyl acrylate (reactive solvent can be used instead of styrene crosslinked unsaturated polyester resins) may affect the mechanical properties of nanocomposite, depending on the treatment of montmorillonite [Kim et al. (2004)]. Nanoclays can also be used to reduce the shrinkage of polyester resins [Shubel et al. (2006)]. The withdrawal is a major drawback of polyester resins, because it causes dimensional changes and distortion of composite parts. The withdrawal of a neighbor virgin resin is lowered from 7.5% to 5.8% with only the addition of 1 wt% clay nanofiller. The breaking strength of a nanocomposite with 4% nanofillers is increased by 108% and Young's modulus of 53%. In contrast, an anti-withdrawal conventionally used such as polyvinyl alcohol (PVA) should be used in higher proportions (about 30%). This causes a decrease in breaking strength and flexural modulus of 24% and 32% respectively. *Application to vinylester resins:* The incorporation of a 4% nanoclay in a vinylester resin slightly increases the modulus of the nanocomposite, but decreases the elongation at break compared to the virgin resin [Chen et al. (2007a)]. Further work on the hybrid resins modified vinylester/epoxy with two different types of clay nanofillers [Karger-Kocsis et al. (2003)] showed that the fracture energy of nanocomposites containing 5 wt% nanofillers was doubled compared to that of pure resin. Chen et al. (2007a) also highlights the importance of surface functions of nanofillers on the final properties of composites. *Application to Epoxy resins:* The breaking strength and elasticity modulus in compression of epoxy resins can be increased by nanoclay (montmorillonite with surface treatment). The wear resistance is also changed (to a 30% increase) but depends on the rate and morphology of nanoparticles. Depending on the rate of nanofillers, it is possible to obtain either a lubricating effect of the surface which protects the nanocomposite or an increase of mass loss by friction [Lin (2007)]. Regarding previous paragraphs, it appears that the mechanical properties of polymers can be greatly enhanced by nanoclays, depending on two parameters:

- The surface treatment of nanofillers is essential to increase the filler/matrix adhesion, otherwise there is no change in the properties of the nanocomposite.

- The dispersion of nanofillers is another governing parameter. It requires considerable energy: vigorous mixing or ultrasonic dispersion

In these circumstances, it appears that for optimum rate of 5% of nanofillers, the characteristics to break can be doubled. Regarding the tensile properties, the results are contradictory depending on the author and resin, with a small increase in elastic modulus and decrease in elongation at break or a 53% increase in elastic modulus and increase of 108% elongation at break.

4.1.2 Nano-oxides

Application to polyester resins: For highly cross linked polyester resins, if alumina nanoparticles (15 nm) are not surface treated, the properties of the nanocomposite are lower than the resin alone [Zang et al. (2007)]. Cons by grafting aminosilanes functions to increase adhesion nanofiller-matrix can increase by 100% the K_{1C} stress intensity factor of a composite for a loading rate of 4.5%. The mechanical properties of unsaturated polyester resin are considerably improved by the incorporation of 4% TiO_2 nanoparticles with an average grain size of 27 nm, only if nanoparticles have a strong adhesion due to surface defects [Xiao et al. (2002)]. The presence of titanium dioxide increases the stress at rupture in traction of 47% and Young's modulus of 22%. It leads to an increase of flexural strength at break of 173% and modulus of elasticity flexion of 22%. The impact strength is increased of about 60% of it. Reference [65] also highlights the breaking strength and modulus of elasticity in compression of epoxy resins can be increased by TiO_2 nanoparticle. *Application to Epoxy resins:* The abrasion resistance of epoxy resins is generally improved by fillers such as graphite, polytetrafluoroethylene (PTFE) or short carbon fibres. A comparison between conventional fillers and / or the incorporation of nanoparticles of TiO_2 indicates that for a content of 5% in volume, the wear resistance of a nanocomposite containing nanoparticles of TiO_2 is higher than that of resin containing the same amount of PTFE (particle size 4 μm) [Zang et al. (2007)]. However the best wear resistance of epoxy resins is achieved by a combination of traditional fillers (15% graphite and 15% short carbon fibres) with TiO_2 nanoparticles (5% by volume). As for nanoclays, dispersion and surface treatments are the governing parameters for the effect of nano-oxides on mechanical properties. Various studies have shown that treated nano-alumina (4.5% by volume) can double the K_{1C} of virgin polyester resins. Nanoparticles of TiO_2 (4% in volume) increase significantly the characteristics of flexural and tensile and impact strength of virgin polyester and the abrasion resistance of epoxy resins.

4.1.3 Carbon nanotubes and nanofibres

Work on strengthening a vinyl ester resin by carbon nanofibres for rates from 0 to 25 wt% [Xu et al. (2004)] features show that flexural modulus and strength decrease with the rate of nanofibres. It should be noted however that the bending tests were conducted only on nanocomposites with nanofillers that have received no surface treatment and therefore with a low fibre-matrix interaction. Xu et al. (2004) also deals with enhancing resins and vinyl ester hybrid resins, vinyl ester/vinyl ester and epoxy-urethane by MWCNT to a rate of 2%. Toughness (stress intensity factor and fracture energy) was slightly increased (+27% and +35%) for an expense ratio of 1% and decreased for higher rates. An important point is that only the outer wall of the MWCNT is coupled with the matrix and therefore the effectiveness of capacity decreases with the number of walls or layers (Walls). Seyhan et al. (2007b) presents the reinforcement of polyester resins by carbon nanotubes, using Double-Wall Carbon Nanotubes (DWCNT) and Multi-Wall Carbon Nanotubes untreated and treated

(grafted amine functions). Nanocomposites comprising a rate of 0.5% of treated nanotubes have tensile properties slightly higher than that of virgin resin, and exhibit an increase of 5% to 17% of the tensile strength. Nanocomposites containing untreated fillers have the same characteristics as pure resin. Carbon nanofibres have also been used to improve resistance to delamination of glass-fibre reinforced polyester composite [Sadeghian et al. (2006)]. The critical energy for delamination crack growth in mode I is increased by 100% to a rate of 1% nanofibres. These studies highlight the need and difficulties of the dispersion of nanotubes in the matrix. Using a three-roll mixer gives better results than commonly used methods such as mixture by stirring or ultrasonic dispersion. The rate of these nanofillers for optimum effect is around 1% and improvements in tensile properties and fracture resistance obtained are low compared to the unique characteristics of these materials. As a known effect, there is the resistance to delamination of a glass-reinforced polyester, which was doubled by carbon nanofibres. Note that these nanofillers must be surface treated so as to improve a characteristic of resins. The dispersion of nanofillers is difficult, critical and requires high shear rates (three-roll mixer).

4.2 Modification of thermophysical properties of composites

All the nanocomposites studied hereafter exhibit anisotropic thermal conductivity. The methods of preparation of composites often direct, intentionally or not, the nanofillers within the matrix. Conductivity measured in the direction of orientation of the nanofillers is therefore higher than the one measured in the transverse direction. The majority of studies concern carbon nanotubes in polymers. For Carbon nanotubes, Vergne (2007) explains that many parameters influence the thermal conductivity of such composites: the contact resistance, the nature, dispersion and orientation of carbon nanotubes, the impurities in the formulation of thermoset resins or synthesis of CNT, the dispersants, nanotube bundles, metal catalysts and carbonaceous residues.

4.2.1 Nanoclays

Very few data are found in the literature related to thermal properties of nanocomposites using nanoclays. Few data corresponding to micrometric clay-based fillers could be found by Al-Malah & Abu-Jdayil (2007) and Abot et al. (2003). They show that increasing the amount of charge (between 25 and 60 wt%) increases the thermal conductivity of the composite obtained. Al-Malah & Abu-Jdayil (2007) justifies this behaviour with the highest thermal conductivity of mineral fillers ($38 \text{ W.m}^{-1}.\text{K}^{-1}$ for Al_2O_3 and $2.7 \text{ W.m}^{-1}.\text{K}^{-1}$ for SiO_2) compared to resins like polyester ($0, 1 \text{ W.m}^{-1}.\text{K}^{-1}$). As a consequence, it remains probably true for smaller fillers. Haque et al. (2002) present the thermogravimetric analysis and DMA of a composite epoxy/glass fibre with 1 to 2wt.% of nanoclays (montmorillonite). The incorporation of nanoparticles increases the glass transition temperature by a few degrees and the decomposition temperature of about 20°C .

4.2.2 Carbon nanotubes

Decomposition temperature: The addition of MWCNT in epoxy resin have no significant influence on the decomposition temperature of the composite. Zhou et al. (2008) has made measurements of decomposition by thermogravimetric analysis under nitrogen at $10^\circ\text{C}.\text{min}^{-1}$ on specimens of epoxy containing 0 to 0.4 wt% MWCNT. Carbon nanotubes of a diameter of 30-50 nm and 3 μm long and the matrix polymer are mixed using a high intensity ultrasound method. All samples start to decompose around 340°C , and are completely decomposed at

460°C whatever the concentration of MWCNT is. *Thermal conductivity*: Works on epoxy/CNT nanocomposites all indicate an increase in thermal conductivity. Biercuk et al. (2002) asserts that epoxy with a charge of % SWCNT correspond to a thermal conductivity increased of almost 125% at room temperature. The influence of mass fraction (ranging from 0.05 to 3.0%) of carbon nanotubes MWCNTs on the thermal conductivity of composite epoxy/MWCNT was studied by Evseeva & Tanaeva (2008) from -150°C to 150°C. The introduction of 0.1 to 1.0% of MWCNTs increases the thermal conductivity of epoxy resin by about 40%. A larger amount of nanotubes is decreasing thermal conductivity, probably due to poor dispersion of nanotubes at high concentrations. Indeed, the specific surface load increases when the size of particles or clusters of particles decreases. However, more specific surface loads are high and their effectiveness on the performance of the nanocomposite is great. *Coefficient of thermal expansion*: Gonnet (2004) studied the variations in coefficient of thermal expansion and glass transition of an epoxy/SWCNT nanocomposite with 1 and 5 wt.% of carbon nanotube. The coefficient of thermal expansion of the composite before the glass transition is lower than average than the epoxy resin alone. It is lower for a mass fraction of nanotubes for a 5% mass fraction of 1%. The coefficient of thermal expansion of the composite after the glass transition is higher than that of the epoxy resin alone. The glass transition temperature of the composite is lower than the resin alone. The glass transition temperature of 5 wt.% nanocomposite is lower than for the 1 wt.%. Dos Santos et al. (2008) noted that the expansion coefficient of epoxy resin remains constant with or without the addition of 0.5 wt% MWCNT, whether before or after the glass transition. Similarly, Yuen et al. (2007) notes that the expansion coefficient of a composite epoxy/MWCNT is not affected if the mass fraction of MWCNT is less than 0.5%. However, its glass transition temperature increases from 167°C for pure epoxy to 189°C for the nanocomposite. According to the literature, the thermophysical properties of these composites vary with the nature of nanofillers, their mass fraction, morphology and dispersion. The thermal conductivity of nanocomposites using thermoset resins always increases with the addition of nanofillers and depends strongly on the nature of the charges, and their concentration and quality of their dispersion. The conclusions are highly variable from one publication to another. The thermal response of these nanocomposites is different from that of similar composites containing fillers of larger size, heat transfer to macroscopic scales and sub-micron being different. The coefficient of thermal expansion, glass transition and decomposition temperature of nanocomposites using thermoset resins decrease with the addition of nanofillers for some authors, while others have almost found the reverse. Given the large number of parameters to which the thermophysical properties of nanocomposite appear sensitive, especially about their implementation, it is difficult to predict a priori the thermal behaviour of such composites without a preliminary study on a case-by-case basis. These studies could examine the evolution of their thermal properties based on influence parameters such as nature, rate, and dispersion of fillers, and look for possible correlations.

4.3 Modification of optical and radiative properties of composites

Amorphous polymers are transparent to the visible range [Trotignon et al. (1989)]. The addition of pigments and fillers increases the light scattering and opacifies the material. Thermosets are generally uncharged amorphous and therefore transparent. In the infrared, the absorption spectra are characteristic of the polymer (molecular vibration modes). The conventional thermoset generally charged have a high emissivity and are opaque. If the polymer is opaque to the considered wavelength and whether the contents nanofillers are small, it is very likely that those of the polymer mainly influence the radiative properties of

the composite. Indeed, in this case the only important properties are the surface properties (reflectivity, thermal emissivity) and the surfaces of nanofillers present on the surface are very low compared to that of the polymer. The effect will be totally different for nanostructured objects, which could behave as metamaterials.

It is possible to maintain the transparent properties of the polymer as the levels of nanofillers are small but sufficient to significantly improve the mechanical properties and heat resistance of the nanocomposite [Bharadwaj et al. (2002)]. For semi-transparent material, transmittance is more likely to decrease with an increasing nanofiller content [Bharadwaj et al. (2002), Thompson et al. (2003)]. Radiation intensity phenomena can be obtained using semiconductor particles, especially nanocrystals.

4.3.1 Nanoclays

According to Bharadwaj et al. (2002), the influence of nanoclay plates (aluminosilicates) depends on the size and shape of particles. The decrease of transmittance is due to scattering and absorption from plates. Authors suggest that transparency is even increased when the dispersion of plates is important.

According to Chrismann et al. (2010), the incorporation of "Organo-modified layered silicates" (OMLS) particles is limited in transparent materials due to the diffusion induced by the excessively large flat surfaces of the plates relative to the thicknesses.

4.3.2 Carbon nanotubes

Because of their highly anisotropic nature, carbon nanotubes are only incorporated in thin films to preserve the transparency of the polymer [Chrismann et al. (2010)] to modify optical properties. The incorporation of 0.5% SWNT (single wall nanotube) in a PMMA film of 20 μm in thickness gives a transmission factor of 46% for visible wavelength of 500 nm .

4.3.3 Nano-oxides

The use of "classic" nano-oxide particles (silica, alumina, zirconia) appears promising for the reinforcement of transparent polymers. In general, these are quasi-spherical nanoparticles that are used in transparent materials to prevent the diffusion phenomena [Chrismann et al. (2010)]. It is possible to produce transparent composite with refractive index or variations index chosen. The use of these materials is limited to the production of special optical components (lenses, optical fibres, waveguides, etc).

Chen et al. (2007c) present the characterization of a nanocomposite polyurethane/ TiO_2 emissivity. Emissivities measured for the band 8-14 μm are: 0.945 for the raw polyurethane, 0.925 for the pure TiO_2 and 0.538 for the composite polyurethane/ TiO_2 . The TiO_2 content in the composite is not clearly stated. It seems that it is possible to generate composite materials with an emissivity, which is considerably lower than the emissivity of individual components. According to the authors, the change in emissivity is due to interfacial phenomena that alter the molecular vibration modes. Lin et al. (2004) present the results of measurements of spectral emissivity on a nanocomposite film polyimide/ BaTiO_3 . Emissivities averages for the spectral band 8-14 μm are respectively 0.703, 0.574 and 0.605 for mass concentrations of particulate BaTiO_3 : 0%, 14.7% and 28.7%. Emissivity variations are due to interfacial interactions. The spectral variations (depending on the wavelength) measured relative to a nanocomposite with 14.7% and 28.7% of BaTiO_3 are similar to those of unfilled polymer. Thompson et al. (2003) announced that the emissivity of a nanocomposite polyimide/indium-tin-oxide is higher than the polymer alone.

4.4 Modification of electrical and magnetic properties of composites

4.4.1 Nano-oxides

Nanocomposite materials consisting of nano-oxide and a conductive matrix paved the way for new applications such as smart windows, new toner, copier, conductive paints and rechargeable batteries [Maeda & Armes (1994), Butterworth et al. (1995), Jarjays et al. (1995), MacDiamid (1993)]. A first class of materials corresponds to the association of π -conjugated polymers with permanent magnetic nanoparticles (Fe_3O_4 , $CoFe_2O_4$, $NiFe_2O_4$). These magnetic nanoparticles exhibit superparamagnetic properties. Each nanoparticle behaves as a nano-magnet. The collective behaviour of magnetic nanoparticles can be greatly affected by their ability to aggregate. Thus, optimal performance can be achieved by dispersing these nanoparticles in a non-magnetic polymer matrix. Nanocomposites containing ferrite and a polyamide (PA) or polypyrrole (PPy) matrix present both interesting electric and magnetic properties [Turcu et al. (2006)]. This allows consideration of multiple applications such as electromagnetic interference shielding or microwave absorbing materials. Other works evoke the dispersion of TiO_2 nanoparticles [Nabid et al. (2008)] or SiO_2 [Dutta & De (2007)] matrices to add conductive or dielectric optical properties to nanocomposites.

4.4.2 Carbon nanotubes

The CNTs are used in π -conjugated polymer matrices to improve significantly the electrical and mechanical properties, and these composites are often denoted NT-CP (Carbon Nanotube - Conducting Polymer) in the literature. These materials exhibit specific properties related to electronic interactions between fillers and the matrix. The electrical properties are enhanced and thus give rise to all sorts of original applications: Schottky diodes, capacitors, high performance electrodes in rechargeable batteries [Chen et al. (2002), Hughes et al. (2002)], nanowires for optoelectronic applications, organic light emitting diodes (OLEDs). Polyacrylonitrile (PAN) [Cochet et al. (2001)], polypyrrole (PPy) [Chen et al. (2002), Hughes et al. (2002), Baibarac et al. (2003)], polythiophene [Philip et al. (2004)] and polyacetylene [Tchmutin et al. (2003)] based nanocomposites are commonly found in research and industrial applications nowadays. Their electrical properties are dependent on the synthesis methods, as it influences interactions between CNT and polymer. Nanocomposite PAN/CNTs exhibit electrical conduction properties that can be described simply as either parallel conductors when the interaction is Van der Waals forces or charge transfer when there are covalent bonds. There is no percolation in these materials. Some studies have concluded that improving the electrical properties of the NT-CP was due to the doping of polymer by nanotubes [Lee et al. (2001), Zengin et al. (2002)].

4.4.3 Metallic nanoparticles

Metallic nanoparticles (NPs) correspond to crystallite metal (Fe, Ag, Au, etc) of spherical shape. The incorporation of such nanoparticles in a conductive polymer matrix allows increasing the electrical conductivity of the composite in a synergical way. The applications are diverse and of interest for many areas: photovoltaic cells, memory devices, anticorrosion coatings, supercapacitors, sensors or catalysts. Thus, a composite of platinum nanoparticles (Pt) or palladium dispersed in a matrix of PPy shows a remarkable electrocatalytic activity. A nanofiller Fe in a polystyrene matrix (insulant) or PPy (conductor) provides a magnetic composite insulator or conductor. These materials are used as electromagnetic shielding for electronic components. A number of studies are devoted to the use of nanoparticles of noble metals (Au, Ag, Pt) often associated with PPy or PAN [Chen et al. (2007b), Bose & Rajeshwar

(1992)]. The objective is to develop nanocomposites for opto-electronics, optical filters or absorbers in different frequency bands by exploiting the properties of nonlinear optical NPs, photonic crystals, materials with high electrochemical properties, and biological or chemical sensors.

4.4.4 Metal-CNT systems

Functionalization of carbon nanotubes by metal ions is also proposed to form wave-absorbing materials. Thus, the CNTs are coated with silver ions [Zhao et al. (2008a)] or nickel [Zhao et al. (2008b)]. Silver nanowire [Zhao et al. (2008b)] or iron [Shi et al. (2003)] could also be encapsulated inside the nanotube. Such epoxy CNT-modified material is capable of absorbing in microwaves range [Zhao et al. (2008b)].

4.5 Modification of gas diffusion properties

The gas and solvent diffusion properties of polymers could be modified using nanofillers, especially when nanoplates are used [Al-Malah & Abu-Jdayil (2007)]. This parameter is essential in some applications such as food packaging. The structure conferred to the polymer when nanoplates are used induces an increase in the distance to be traveled by gases between plates. This distance is qualified by the "tortuosity" (deviousness) factor (Fig. 6). It is especially present with nanocomposites using nanoclays, and depends on dispersion, diffusion, exfoliation and the orientation of the plates. Improved barrier properties of gas transfer is related to the parallel orientation of organo-modified nanoclay plates, and therefore requires a high degree of exfoliation. This property will lead to the creation of new food packaging materials, as oxygen diffusion is one of the governing parameters of food conservation.

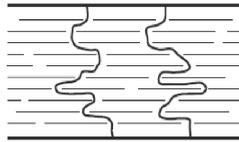


Fig. 6. Tortuosity for gas diffusion properties of lamellar nanocomposite

4.6 Modification of fire behaviour of composites

Materials used to meet performance criteria against fire involve the use of additives to improve their behaviour. To meet the specifications in terms of choice of materials, new systems to improve the fire behaviour of polymers based on the introduction of nanofillers can become an alternative to traditional ways. Since the first studies on organomodified clays [Giannelis (1996), LeBaron et al. (1999)], various studies have highlighted the interest of various types of nanoparticles (nano-oxides [LeBaron et al. (1999)], polyorganosiloxanes [Finaa et al. (2006)], carbon nanotubes [Peeterbroech et al. (2007)]) or natural (organo-modified phyllosilicates, delaminated talc, kaolin submicron [Le Bras et al. (2005)]). A synergy between classical flame retardant and nanofillers may be interesting as it may decrease the amount of flame retardant and thereby reduce the loss on other properties (including mechanical). Extensive details on fire behaviour of nanocomposites could be found in Morgan & Wilkie (2007) and Morgan (2009). Gilman (1999) and (2000) has demonstrated that the nanoclays particles brought a significant improvement in the flammability properties

of the polymer within which these were dispersed. This enhanced fire resistance is attributable to the formation of a compact and superficial layer of clay shells during the exposure to flames, which thus act as a thermal barrier. The fire behaviour of the matrix will obviously be dependent upon the way the nanocomposites fillers are dispersed within such matrix. Fillers should be evenly dispersed to confer flame-retardant properties. The mechanism of action according to which the nanoparticles confer flame-retardant properties is attributable to the accumulation of inorganic material upon the composite surface together with the formation of char. This shield will reduce the material and heat transfers between the flame and the polymer. It then reduces the radiative flux directed towards the substrate by diffusing the incident radiation towards the gaseous phase and as a result, limits the degradation rate of the material [Gilman (2000)]. The organophile montmorillonite clays generate improvements in the mechanical properties without losing impact strength. An even or perfect dispersion of clay, i.e. an exfoliated structure, will show an important increase in the stiffness of the composite material for low load rates. The synergy existing between the traditional reinforcements, such as glass fibres and nanoclays is of particular interest. The association of glass fibres and montmorillonite produces a much more rigid material with a larger temperature range than the traditional composite material that has the same reinforcement rate. The effective flame retardancy is obtained by combining the nanoparticles effect with conventional flame-retardants such as metal hydroxides, phosphorous or halogenated compounds. Their mode of action is based on physical mechanisms and physico-chemical properties [Le Bras et al. (2005)]. The large majority of nanocomposites defined for their fire behaviour properties use nanoclays. The barrier effect of layered nanoparticles (nano-clay) corresponds to two effects:

- Limiting the transfer of volatile fuel gas flow associated with the decomposition of polymer,
- Limiting diffusion of oxygen inside the material.

The formation of a particulate barrier is related to the mobility of particles toward the surface exposed to the external heat source as well as the removal of polymer decomposition. The incorporation of nanoparticles also tends to generate an increase in viscosity, which limits the heat and mass transfers in material. The presence time increased in the condensed phase decomposition products of the polymer facilitates dehydrogenation reactions catalyzed by the large area of nano-particles, leading to the formation of condensed structures charred (char) that grow on the surface of residual material. Furthermore, incorporation of nanotubes in EVA also showed a greater presence of free radicals in the combustion residue. The way of thermal decomposition of the polymer tends to be modified in the presence of nanoparticles, with a slowed emission of volatile fuel, even in the absence of conventional flame retardant. However, a fraction of the nanoparticles could be released into the atmosphere during combustion [Laachachi (2005), Chivas-Joly et al. (2010)]. The use of double-layered hydroxides is an alternative to the use of cationic clays for making epoxy-based composites with good fire properties [Ibeh et al. (2006)]. The cone calorimeter results on vinyl esters containing clays (Cloisite 15 A) or POSS highlighted a reduction of maximum heat release rate and increase of time to ignition, but no modification on total heat released [Chigwada et al. (2005)]. A combination with a phosphorus-based flame retardant promotes a greater improvement. Table 2 presents results obtained by various authors, using nanoclays in thermoplastic and thermoset polymers. Common compositions between classical flame-retardants and nanoparticles that have a synergy effect are:

	Nanofiller used	Polymer matrix	Effect on fire behaviour on cone calorimeter test (in comparison with polymer alone)
Chigwada et al. (2005)	Montmorillonite (Cloisite 15 A)	Vinylester, Bisphenol A/epoxy,	Decrease of maximum heat release rate
	Montmorillonite (1%, 3% and 5%)	PS, HIPS, ABS, PE, PP	Decrease of maximum heat release rate
	Montmorillonite (1% and 2%)	PA6	Increase of ignition time, Decrease of maximum heat release rate
Kandola (2008)	Montmorillonite (Cloisite 25 A) (5%)	Polyester	Increase of ignition time, Decrease of maximum heat release rate
		Polyester + APP	Increase of ignition time, Decrease of maximum heat release rate, Increase of smoke released
Gianelli & Camino (2006)	Montmorillonite (5%)	Polyester	Decrease of maximum heat release rate
Hussain et al. (2004)	Montmorillonite	Phosphorous-modified epoxy resin	Decrease of maximum heat release rate

Table 2. Effects of nanofillers on fire behaviour of various nanocomposites.

- Organo-modified nanoclays in combination with metallic hydroxides, e.g. aluminium trihydrate (ATH) or magnesium dehydrate (MDH);
- Organo-modified nanoclays in combination with phosphorous compounds, to form intumescent structure, e.g. Ammonium polyphosphate (APP);
- Nano-hydroxides and nano-oxides in combination with phosphorous compounds (APP, phosphinates);
- Carbon nanotubes in combination with metallic hydroxides.

Pyrogenic silica and nanoalumina produce synergistic effects in combination with ammonium polyphosphate [Cinausero (2009)]. The use of treated silicas (octylsilane) enhances the performance of the system at constant composition flame retardant. Improving the fire behaviour of polymer materials using nanoparticles is related to the existence of barrier effects, but also catalytic process and capture of radicals. The incorporation of nanoparticles can advantageously be combined with the reactive flame-retardants.

5. Perspectives

Nanoscale dimensions can increase significantly the physical interactions, physico-chemical and chemical interfaces in materials. The morphologies obtained for the nanocomposites and the ability to modify the interfaces are essential to maximize the properties. For all charges, surface treatment and mixing are key points dictating the performance of nanomaterials. The variety of combinations between nanofillers, matrix and classical additives allow wide possibilities of material specifications improvements: mechanical, thermal, optical, electrical properties as well as reaction to fire.

The improvement in the quality of fillers (e.g. less catalyse residues in carbon nanotubes) and progress in production processes will lead to an increasing diffusion of such nanocomposites in a wide range of applications with strong requirements.

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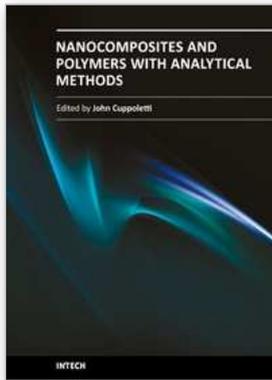
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Phone: +385 (51) 770 447
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Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821