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Thermal degradation, flammability, and potential toxicity of polymer nanocomposites

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Abstract: Many new nanomaterial-based products have been developed recently, due to advances in nanotechnology. These are designed to offer new functionalities or to modify existing products. This chapter examines the thermal degradation and flammability of various nanocomposite polymers and the potential risks of burning them. Different fire scenarios have been simulated with a cone calorimeter coupled with FTIR, condensation nuclei counter (CNC) analysers, and/or cascade impactors in order to produce aerosols emitted at different radiation levels and flammable atmospheres. The testing conditions and influential parameters are presented. Combinations of pristine ultrafine particles with soot or other ultrafine particles during thermal degradation can directly affect human health. Hence, more research is needed into the morphology and composition of the released nano-objects and ultrafine particles.

Key words: engineered nanomaterials, nanoparticles, health safety, environmental effects, release and exposure, sampling protocols, nanoproduct life cycle analysis.

13.1 Introduction

This chapter addresses data and research into the thermal degradation and combustion behaviour of various nanocomposites, particularly those studied in the authors' Nanofeu (supported by the French Research Agency (ANR)) and Innanodep projects (supported by the French Environment and Energy Management Agency (ADEME)).^{1,2} The innovative coupling of techniques used in these projects to investigate the morphology and composition of ultrafine particles released by combustion is then described. Finally, both the potential toxicological risks resulting from the inhalation of released gases and pristine nanoparticles and the initial results from the use of the above described characterization techniques are detailed.

Nanoparticles are generally present in the environment. There are three main categories: naturally occurring, anthropic, and engineered nanomaterials. Naturally occurring nanomaterials include volcanic ash, ocean spray, bacteria, and natural minerals. Anthropic nanomaterials correspond to the ultrafine particles

emitted by the combustion of fuels or waste (e.g. diesel particles, fly ash), transportation (e.g. abrasion of tyres or brakes), and industrial activities (e.g. silica fumes). Engineered nanoparticles (ENP) can be divided into two further categories depending on their incorporation in polymers.

Nanoparticles that haven't been used recently are referred to as 'historical'. In particular, these include carbon black, which has been produced in China for centuries using the Lamblack process, and silica, produced by either the pyrogenated or precipitated process.³ The behaviour of these materials and properties of their polymer composites are relatively well understood. Surveys into the health of workers in the industry have collected a lot of data about the potential adverse effects of these nanoparticles.^{4,5} There have also been several studies into the thermal degradation of the corresponding nanocomposites for many polymer matrices. In contrast, research is ongoing into the potential toxicological effects of newly developed ENPs, such as metals and oxides at the nanometre scale, carbon nanotubes, and organomodified layered silicates, and into the thermal degradation of corresponding nanocomposites. In particular, more research is needed into the composition of the particles, nano-objects, and gaseous products released by the combustion of nanocomposites. This is especially important given the increasing use of nanocomposites in plastics.⁶

Although it is possible to avoid the release of nanoparticles during the production process to a significant extent by using the relevant metrology,⁷ the useful life stage of products containing nanoparticles and, in particular, their waste stage, have the potential to be a source of nano-objects or ultrafine particles containing the initial nanoparticles. Release during the useful life stage can be discounted assuming that nanoparticles would be firmly coupled to the polymer matrix by then. However, there are exceptions to this, such as abrasion or machining, thermal or UV ageing, action of chemical agents, and in particular accidental destruction in a fire. The waste stage, on the other hand, will soon become the main source of free nano-objects, since large quantities of nanocomposites are likely to end up in municipal solid waste incineration (MSWI) plants. Incineration, instead of recycling, will probably become the most convenient way to dispose of plastics containing nanoparticles, since it is difficult to identify nanocomposites and to reclaim high-performance composites for use in sports equipment, clothing, and coatings. However, it appears that waste incinerators can only partially remove the ultrafine particles corresponding to the nanometre range from the gaseous effluents. It is therefore necessary to examine the thermal degradation pathway of nanocomposites in the case of intentional or accidental combustion. The nature of particles, nano-objects, and gaseous emissions needs to be identified, taking into account the type of nanoparticle, its surface modifications, and its polymer matrix. The potential risks to human health and the environment must then be assessed, with respect to the possible interactions between nanoparticles and decomposition products of the polymer as well as the intrinsic toxicity of the nanoparticle initially incorporated in the polymer.

13.2 Thermal degradation processes of polymers and nanocomposites

The absence of recycling methods for most nanocomposites means that incineration is usually used to dispose of products when necessary. Incineration processes impose a high temperature quickly, resulting in pyrolysis mechanisms. Pyrolysis breaks up many of the chains that form polymers. If temperatures are sufficiently high to cause polymer degradation (decomposition) and volatilization, the combustion produces fuel. This fuel moves to the surface of the specimens through convection phenomena (bubbles), and the gases mix. The polymers are ignited when the gas phase concentration of fuel, produced by thermal decomposition of macromolecules, reaches the lower flammability limit. In these conditions, a flame can be caused by an external ignition or by self-ignition, provided the gas phase is above the self-ignition temperature.⁸

Before ignition, oxygen controls thermal decomposition of the top layer of the specimens, whereas pure thermal degradation may occur in the liquid below. The significant contribution of thermo-oxidative decomposition to the fuel production prior to ignition supports previous observations about the combustion behaviour of polymethylmethacrylate (PMMA) and polystyrene by Kashiwagi and Omori.⁹ However, after ignition, oxygen will be limited or unavailable, as it is mainly consumed by the flame at the surface, thus a higher temperature is required to produce the same fuel flow.⁸

To improve the thermal, mechanical, and other properties of the organic polymeric materials, inorganic fillers are added to the polymer formulations. This forms organic-inorganic composites. The properties of a composite material depend on the properties of its individual components. The phase morphology and interfacial properties of the composites also significantly influence the properties of the composite material.¹⁰ Over the last 15 years, studies of the formation of nanocomposites have been motivated by interest in their high interfacial areas and exceptional properties. Organo-modified layered silicates, nano-oxides, and carbon nanotubes^{11–18} are the main dispersed components of nanocomposites.

When incorporating nanoparticles into the polymer matrix, both the physical properties of the polymer (e.g. melt viscosity) and chemical decomposition mechanism may be significantly modified. Thus, polymer nanocomposites exhibit a different ignition behaviour compared with their reference polymer. Surface temperature profiles suggest that ignition may be controlled in nanocomposites. This can be done using nanoparticle-catalysed oxidation of the gases, which are generated at the surface of the condensed phase due to volatilization of the polymer, or by forming a protective layer at the first stages of matrix degradation. This means that conditions for ignition can be created as soon as the polymer decomposition temperature is reached. This contrasts with pristine polymer, in which enough volatiles from bulk polymer pyrolysis have to be produced and mix with the air above the specimen to reach the lower flammability limit.⁸

In general, the thermal degradation of polymers occurs through the following mechanisms:

- Random scission¹⁹
- Side group scission^{20,21}
- Monomer reversion¹⁹
- Other mechanism and re-arrangements.^{22,23}

A global scheme has been proposed by Stauffer (Fig. 13.1).²⁴

The mechanism of *side group scission* may induce the formation of aromatic gases, such as benzene, toluene or styrene, in just seconds. These gases are very different from the polymer structure, as opposed to the first gases released, which correspond to the side groups (for example, hydrochloric acid is released from polyvinyl chloride).

The depolymerization mechanism is equivalent to monomer reversion and is more easily identifiable. However, it is linked to the temperature at which pyrolysis occurs. Below 500 °C, the monomer is the only product released, whereas at higher temperatures, other bonds can be broken and yield other radicals.²¹ In the case of *random scission*, the polymer backbone is broken apart randomly, since all C–C bonds have the same strength. Smaller products, like alkanes, alkenes, and alkadienes, are formed.¹⁹

A polymer does not always undergo only one of these routes of pyrolysis. The types of reaction are partially determined by the strength of the bonds in the molecule. The bond that is the most easily thermolysed or broken will be favoured.²⁵ For example, the chain is likely to break at a point of instability such as a highly substituted carbon atom (tertiary or quaternary). One of the most important parameters determining the reaction is the temperature at which pyrolysis occurs. As temperature increases, the production of radicals and molecules decreases.²¹ While the proportions of the products may change, the types of products are similar.

13.3 Thermal stability of nanoparticles

Many nanoparticles such as various nano-oxides (Al_2O_3 , TiO_2) can be considered inert, given the maximum temperatures generally attained by polymers in a fire or in the furnace of an incinerator. The nanocomposite therefore forms a residue. Other nanoparticles can be partially or totally oxidized, depending on the oxygen diffusion through the nanocomposite as it decomposes due to exposure to a heat source.

Depending on the combustion conditions, carbon-based particles can be destroyed, pyrolysed or even remain intact if they are able to form a thermal shield, as carbon nanotubes can.²⁶ PolyOrganoSilsesquioxanes are made up of siloxane cages linked to organic groups.²⁷ In their case, thermal decomposition mainly leads to the release of organic compounds corresponding to these groups, but also to silica.

13.1 Polymers and their approximate classification according to the degradation mechanism.²⁴

Various nanoparticles may react with gases released by the thermal degradation of polymers or additives in incinerators (see section 13.6). Some nanoparticles can also lose mass due to water release from hydroxyl groups present at the mineral surface (e.g. silica, or layered silicates such as kaolinite, halloysite or sepiolite), due to bond water (e.g. hydroxides such as AlOOH) or due to the thermal degradation of their surface agents (e.g. organomodified layered silicates (OMLS)).

The mass loss caused by water release in oxides is generally limited to a few percent of the initial mass of oxides. However, in the case of hydroxides incorporated into polymers for flame retardancy, it can range from 15 wt% for boehmite (AlOOH) to more than 30 wt% for aluminium trihydroxide or magnesium dihydroxide. In addition, the temperature decomposition range of these hydroxides has to be compatible with that of the polymer decomposition, and the onset temperature of water release has to be higher than the processing temperature of the polymer. Owing to these limitations, few types of hydroxide (the three above and also different structures of layered double hydroxides²⁸) can be used at the nanometre scale. These nanometric or submicronic hydroxides have begun to be used in flame-retardant systems. They increase reactivity, due to their large specific surface area, and can contribute effectively to the formation of a cohesive protective layer in combination with other flame-retardant components,²⁹ such as the corresponding micronic hydrated minerals. The increase in reactivity can result in a modification of the temperature range profile of water release. Nevertheless, their very small size seems more influential on fire retardancy than their water content.³⁰ They can also promote the formation of new phosphorous species (e.g. metallic phosphates or phosphinates), such as when alumina, silica or titanium dioxide are combined with ammonium polyphosphate.^{29,31,32} The formation of these kinds of compound can also result in a cohesive barrier, preventing the residual polymer material from decomposing further.

Organomodifiers of OMLS are mainly broken down using the Hoffman degradation reaction (Fig. 13.2), since modifications of montmorillonite or bentonite clays are generally performed using alkylammonium ions. Thermogravimetric analysis (TGA) experiments can be used to show that the organic fraction in OMLS can reach more than 30 wt%, depending on the nature of the alkyl ammonium ion.

13.2 Hoffman degradation reaction of alkylammonium ions.

Table 13.1 Examples of organic modifiers with enhanced degradation temperature in comparison with current alkylammonium ions

Notation	R ₁	R ₂	R ₃	T _{onset} (°C)	T _{pic} (°C)
DMPIM-Cl	methyl	methyl	propyl	259	299
DDMIM -Cl	decyl	methyl	methyl	255	294
DMHDIM-Br	methyl	methyl	hexadecyl	250	304
DMEiM-Br	methyl	methyl	eicosyl	260	315
DMEtBIM-Br	methyl	methyl	ethylbenzene	275	330

The degradation of organic modifiers at around 250 °C leads to acidic clay surfaces which can cause catalytic processes. However, if this happens during the processing steps, it can impede the dispersion of clay platelets, and thereby hinder the formation of nanometric morphology for the composite.

Several studies have used other organic ions as modifiers such as phosphonium, imidazolium, and stilbonium ions.³³ These modifications allow increased resistance to heat sources for the corresponding polymers (Table 13.1). Nevertheless, the high cost of these modifications can outweigh the benefits.

According to Beyer,³⁴ nanocomposites and the pristine polymer usually exhibit similar smoke and CO production. The improvement of fire behaviour is therefore likely due mainly to a change in the combustion process in the condensed phase than to a modification of the nature of the gases produced. This proposition was supported by Gilman *et al.*³⁵ and by Wang *et al.*³⁶ Several theories have been proposed for the mechanism of action of nanoparticles on combustion behaviour. It has been suggested that the polymer first becomes a gas, so that there is a gradual increase in concentration of the nanoparticle at the surface.³⁷ The nanoparticle then moves towards the surface by migration or convection.³⁸ Finally, nano-confinement results in brush structures.^{39,40} Anisotropic nanoparticles, such as nano-clays (organomodified layered silicates) and carbon nanotubes, form a protective layer on the surface of a polymer during combustion or pyrolysis.^{41–43} This protective layer shields the underlying polymer from the external heat flux and reduces the volatilization rate of fuel gases by preventing bubbles from escaping in the polymer melt.

Zhang *et al.*⁴⁴ have shown, for polyamide 6 (PA6) with nanoclays, that the heat flux ratio tends to be independent of heat flux itself and initial sample thickness but

instead depends on the amount of nanoparticle present on the surface. Here the heat flux ratio is the ratio between the imposed heat flux on the surface, when there is no protective surface layer, and the heat flux imposed on the char–virgin interface. The ratio is determined from experimental mass loss data using a numerical model.⁴⁵ Pramoda *et al.*⁴⁶ have also studied the thermal degradation of PA6 with nanoclays. These authors showed that the main gas products produced were cyclic monomers, hydrocarbons, CO₂, CO, NH₃, and H₂O, both for pristine and filled PA6. The presence of nanoclays did not change the decomposition route in a nitrogen atmosphere. Zhong *et al.*⁴⁷ confirmed this observation, through a calculation of apparent activation energy. They found a similar tendency in nanocomposites and pristine polymers. However, they also noticed an apparent need to increase the activation energy of the nanocomposites in an air atmosphere. However, this atmosphere may induce changes in their affinity with the matrix due to oxidation processes. This can promote migration of nanoparticles towards the surface. Hence, their thermal stability and combustion behaviour could be enhanced.

Jang and Wilkie⁴⁸ have investigated the products and residues of polystyrene and polystyrene nanocomposites as a function of OMLS content, using TGA or Fourier transform infrared (FTIR) spectroscopy. They found that the degradation pathway of polystyrene changed because OMLS formed a protective layer at the surface, acting as a barrier to heat and mass transfer. In the presence of clay, additional products are evolved through radical recombination reactions and extensive random scission followed by beta-scission, and hydrogen abstraction. These reactions become significant at a higher concentration of clay because the clay layers retain the degrading polymer while permitting further reaction.

To improve their performance, flame retardants and nanoparticles are frequently used in polymers. This can lead to modification of the composition of fire effluents, and therefore of the potentially toxic gases evolved. The composition of gases produced by the fire depends partly on the combustion conditions (oxygen concentration, temperature ramp, and final temperature) in the gas phase but mainly on local conditions (oxygen concentration and thermal balance) in the condensed phase.⁴⁹ A cone calorimeter coupled with an FTIR gas analyser in a controlled atmosphere can be used to study the solid and gas phase processes occurring during the thermal degradation of polymeric material in general. Results have shown the thermal degradation and gases released strongly depend both on oxygen concentration and irradiance level (or temperature).⁵⁰

13.4 Instrumentation and techniques to investigate degradation products of nanocomposites

This section describes the experimental measurements used to determine the decomposition products of nanocomposites. Physical and chemical characterization of materials (aerosols and gases) can be researched using suitable techniques.^{51–54} The following techniques will be considered:

- TGA coupled with FTIR spectroscopy.
- Cone calorimeter (CC) instrumented with FTIR.
- Condensation nuclei counter (CNC) described by the ISO/DIS 29904 (2012)⁵⁵ standard.
- Low pressure cascade impactor (DLPI: Dekati low-pressure cascade impactor, Tampere, Finland).

13.4.1 Coupling of chemical analytic methods with thermal analysis

Experimental investigations into thermo-chemical analyses are generally conducted through TGA coupled with an FTIR spectroscopy gas analyser, chromatography (GC), and mass spectroscopy (MS). Coupling TGA with various gas analysers provides additional information for understanding the mechanisms of trace element release and reaction kinetics.⁵⁶ The focus will be on these measurement techniques in which very small samples (a few milligrams) are used to investigate heat and mass transfer effects. TGA data are combined with information from FTIR gas analysis instruments.⁵⁷ These testing procedures allow us to measure the mass loss, the heat absorption or the development of the polymer matrix, caused by the chemical changes when the material is heated in an oxidant or inert atmosphere. TGA combined with FTIR is mainly used to establish the behaviour in the solid phase through mass loss measurement. Gas analysis allows us to identify the chemical products released in the solid phase. It provides qualitative and quantitative information about the reaction, which takes place in a heated solid.^{58,59} TGA-GC/MS can be applied to provide information about the mechanism of the thermal degradation steps of nanocomposites. The coupling of data allows us to determine a decomposition mechanism in line with the chemistry of the processes.

The gas analysis method using FTIR has been used in the field of fire safety following the SAFIR⁶⁰ European research programme. This programme has helped to determine the ISO 19702 standard.⁵¹ It consists in sampling gas through one measurement cell and recording the spectral response, generally in the frequency range of 650–4000 cm⁻¹. At each frequency, the position of the absorption bands and their intensity allow determination of the nature and the quantity, respectively, of the present species.

In addition, FTIR can be calibrated for a large range of nanocomposites and used to quantify these species simultaneously. Examples of such species include: H₂O, CO₂, CO, HCl, HF, HBr, SO₂, HCN, NH₃, NO, NO₂, and acrolein.^{61–63}

13.4.2 Coupling of analytic physics methods with cone calorimetry

Often, chemical techniques are coupled with physical characterization techniques to determine information about the collected particles. The combustion model

used is the cone calorimeter. The cone calorimeter has been described in the ISO 5660-1 standard.⁶⁴ It can quantify material flammability characteristics, including time to ignition, heat release rates, mass loss rate, critical heat flux, smoke opacity, thermal response parameters and enthalpies such as vaporization, gasification, and combustion. The test method uses a specimen the same size as the cone calorimeter with a surface area of $100 \times 100 \text{ mm}^2$. A truncated cone-shaped heater exposes the specimen to a constant irradiance level (up to 100 kW/m^2). A spark plug above the test specimen ignites any flammable gases. The effluents are then collected in a hood and transported through a duct coupled with an FTIR, to measure the concentration of submicronic particles (CNC: condensation nuclei counter), and a low-pressure impactor DLPI (Dekati low-pressure impactor) (Fig. 13.3).

The particles can be classified using a low-pressure cascade impactor technique. Mass size distributions and particle number concentrations can, for example, be obtained by using a DLPI or the more advanced electrical low-pressure impactor (ELPI). The aerosol enters the inlet cone and cascades through the orifices, which successively decrease in diameter, with increasing velocities. At each stage of the instrument and each orifice, a high-speed jet is produced and deviated by 90° so that particles with sufficient inertia will extract themselves from streamlines and impact on a collection surface. The orifice diameter decreases from the first to the last stage of the impactor, so that particles 'unimpacted' at stage n are slightly more accelerated at stage $n+1$ towards a new collecting surface. The inertia of a particle is a function of its shape, density, and speed. The shape and density of a particle are unknown in most cases for a given aerosol. Particle size at each stage of the impactor is therefore expressed through an aerodynamic diameter. The density of the particle is thus considered to be equal to 1. Each stage of the impactor is characterized by a 'cut-off size', also called $D_{50\%}$. The 'cut-off size' corresponds to the aerodynamic diameter of particles trapped with an efficiency of 50% on a given stage.

Another way to characterize a stage is according to its geometric mean diameter: the square root of the product of the cut-off size of the given stage and that of the previous stage. The cut-off size ($D_{50\%}$) is related to the Stokes number (i.e. particle inertia) that gives 50% collection efficiency. An impactor plate, therefore, does not have perfect collection characteristics, and thus some under-sized particles are collected and some over-sized particles are admitted to the next plate.

The aerodynamic diameter of an arbitrary particle is equal to the diameter of a spherical particle, with a density of 1 g/cm^3 , which has the same inertial properties in the gas as the particle of interest. An advanced cascade impactor, such as a low-pressure impactor, consists of several such impaction plates with nozzles of gradually decreasing diameters. This equipment classifies inert particles by size, with diameters ranging from 30 nm to $10 \mu\text{m}$. The sampling flow rate recommended by the manufacturer is 10 L/min . The impactor can be

Airborne nanoparticle sampling and characterization

Experimental approach at LNE

13.3 Experimental approach to measure the mass distribution and the number concentration of the produced aerosol with a cone calorimeter (according to standard ISO 5660-1).³⁶

heated, using a thermoregulated device. In previous studies,^{2,65} the temperature of gases at the exit of the apparatus has been adjusted to 40 °C. To perform an isokinetic sampling, the sampling probe is equipped with a nozzle, with an inner diameter of 9.5 mm. At the last stage of the impactor ‘stage 1’, the pressure is reduced to 10 kPa. Due to Brownian motion, which is influenced by thermal agitation, suspensions of aerosols are entrained by random diffusion kinetics. In a cascade impact situation, particles impacting each stage are exposed to several phenomena, including:

- *Diffusion*: in this case, small particles (nanometer size) move, by diffusion, faster than larger particles (micrometre size).
- *Coagulation*: this depends on concentration and diffusion rate and is the most important phenomenon governed by high concentration and small particles. Elementary particles then agglomerate in a disordered way, form larger particles through Van der Waals interactions, and build up a complex structure that can reach several micrometres.

The effect of the particles is partly related to their size. It is therefore crucial to know their distribution by size rather than the total number of particles, especially since this determines their potential direct effects on human health. Measurement techniques are adapted according to the accuracy desired. Table 13.2 shows the different techniques for investigating the degradation products of nanocomposites that can be used and their standard or experimental conditions.

Table 13.2 Experimental techniques available to measure gases and aerosol combustion

	Apparatus	Standard and experimental conditions
Thermal analysis	Thermo-gravimetric analysis (TGA)	At 10 °C/min up 50 to 900 °C under inert atmosphere, few mg of sample
Fire model	Cone calorimeter (CC)	ISO 5660-1:2002 Reaction to fire tests – heat release, smoke production and mass loss rate – Part 1: Heat release rate (cone calorimeter method). Air flux 24 L/s, heat flux in kW/m ² and %O ₂
Gases characterization	Fourier transform infrared spectroscopy gas analyser (FTIR)	ISO 19702:2006 Toxicity testing of fire effluents – guidance for analysis of gases and vapours in fire effluents using FTIR gas analysis Gases (CO, CO ₂ , HCN, HCl, HBr, NO, NO ₂ , CH ₂ CHCHO, HF, SO ₂)

(Continued)

Table 13.2 (Continued)

		Apparatus	Standard and experimental conditions
Aerosol characterization	Direct	Aerodynamic particle sizer (APS 3321-TSI)	Aerodynamic diameter $0.6\mu\text{m} < d_{ae} < 20\mu\text{m}$ $C_{\text{max}} = 5 \cdot 10^3 \text{ p/cm}^3$
		Scanning mobility particle sizer (SMPS)	Differential mobility analyser (DMA)
		Nano ID de Naneum	Condensation particle counter (CPC)
	Indirect		Sampling by diffusion – impaction: $2\text{ nm} < d_p < 30\mu\text{m}$
		Nanometre aerosol sampler (NAS-TSI)	Sampling by electrophoresis: $2\text{ nm} < d_p < 100\text{ nm}$
		Low-pressure cascade impactor (DLPI)	Impaction: DLPI Dekati (ISO DIS 29904)
	Analytical methods	Atomic force microscopy (AFM)	AFM Veeco Nanoman V particles morphology Under air, tapping mode
		EDX (chemical composition)/ Fluorescence X and diffraction X	Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample
		Scanning electron microscopy (SEM)	Zeiss Ultra Plus FEG SEM with STEM and EDX detector Or QUANTA 200FEG (FEI Compagny) Hitachi S-4300 SEM

The aerosol component in fire effluents can be sampled as a whole on a planar filter or a grid, or sampled with an impactor to separate the different particle sizes. After sampling, particles can be characterized chemically, both on the whole sample on planar filters, or on the filter at a given stage of the impactor. As part of this characterization, the nature of the collection surface is the main parameter driving the analyses. If the particle size analysis shows the presence of a poly-dispersed aerosol, it is important to determine whether the different populations have different chemical composition. Some combustible particles contain mineral fillers that can be traced in aerosol, such as titanium dioxide, silica, aluminium trioxide, and clays. Deposits on collection filters can be characterized using X-ray fluorescence. This allows a semi-quantitative analysis of elements and of crystalline structures present at the surface of the filters to be determined. Scanning electron microscopy (SEM)

13.4 AFM technology at LNE.

micrographs with X microanalysis can also be used to obtain information for elementary analysis. To investigate the morphology of particles collected by the cascade impactor coupled with the cone calorimeter fire model, an atomic force microscope (AFM) or a transmission electron microscope (TEM) could be used:

- A transmission electron microscope is used for direct size characterization of fine particles. Particle shape is also determined by TEM examination using a computer interface. Both SEM and TEM involve the examination of particle images. The kind of microscopy used depends on the size ranges of interest; for TEM, the range is from the nanometre up to the micrometre ($0.001\ \mu\text{m}$ to $1\ \mu\text{m}$).
- An atomic force microscope can be used (Fig. 13.4) as follows:
 - (a) After the fire test, glass cover slips are placed directly on the collection surfaces of each impactor stage.
 - (b) These cover slips are imaged using the AFM (P-517 stage and E-710 controller from Physik Instrumente) and a modified head (from Park Systems).
 - (c) AFM images are collected in air using silicon cantilevers from nano-sensors operating in intermittent contact mode. The cantilevers are $125\ \mu\text{m}$ long, have a resonance frequency of 204–497 kHz, spring constant of 10–130 N/m and a nominal tip radius of curvature 5–10 nm.
 - (d) Images are obtained using a specific discrete scanning mode. For each image pixel, the stage moves to the targeted position and waits a very short time for setup stabilization (a few milliseconds to tens of milliseconds). The AFM controller (also homemade) then receives the topographical and phase signals at high frequency (about 250 kHz). The measured points are

averaged to define one pixel of the topographical or phase image. This kind of very slow scanning (it takes about 3 h to acquire 1000×1000 pixels with a stabilization time of 10 ms between each pixel) allows us to take advantage of the very high setup stability in order to calculate a temporal average of the different acquired signals. This in turn enables us to increase vertical resolution without losing the spatial one because the stage is immobile during the acquisition.

13.5 Fire toxicity of degradation products of nanocomposites and its assessment

Understanding the toxic effects of fire effluents is of the utmost importance, since it has been shown that most deaths during a fire result from the inhalation of toxic compounds.⁶⁶ Moreover, the presence of ultrafine particles in effluents may entail high levels of smoke opacity, limiting the ability to escape from buildings.⁶⁷ The inhalation of submicronic particles released from accidental fires or intentional nanocomposite combustion (e.g. in incineration plants) can also constitute a respiratory hazard due to the nature of the particles deposited in the respiratory system. Gases issued during the combustion of plastics and polymer composites contain totally or partially oxidized species (NO_x , CO_2 , CO , SO_2) and products of polymers and additives, such as aliphatic and aromatic hydrocarbons (low compounds, monomers, and oligomers). Other stable compounds are formed such as HCN, halogenated acids. Toxic combustion gases can be separated into two categories: asphyxiant and irritant. The former corresponds to gases that hinder oxygen from reaching the cells and organs, leading to a loss of consciousness and then death. The latter causes incapacitation, including irritation of the eyes and upper respiratory tract. Irritant gases can also cause subsequent lung damage. A list of the main asphyxiant and irritant gases, according to ISO/TR 9122-1⁶⁸ and Blomqvist *et al.*,⁶⁹ is presented in Table 13.3.

The composition of the combustion atmosphere, particularly the CO/CO_2 ratio, depends on the O_2/fuel ratio,⁷⁰ which is defined as follows (equation 13.1):

$$\Phi = (\text{kg fuel/kg air})_{\text{actual}} / (\text{kg fuel/kg air})_{\text{stoichiometric}} \tag{13.1}$$

In the presence of CO, the formation of carboxyhaemoglobin impedes the transport of oxygen from the lungs to the body. From 10 ppm, even over short

Table 13.3 Main asphyxiating and irritant gases

Asphyxiant gases	Irritant gases
Carbon monoxide Hydrogen cyanide	Acetaldehyde, acrolein, benzene, crotonaldehyde, hydrogen bromide Hydrogen chloride, hydrogen fluoride, nitrogen dioxide, phenol, sulphur dioxide, toluene

periods of exposure, impairment of judgement and perception can occur. Exposure to 1000 ppm entails rapid death. HCN can be formed by complex decomposition reactions of polymers containing nitrogen, such as polyamides or polyurethanes, as well as from natural fabrics, such as wool and silk. This gas is approximately 25 times more toxic than CO because it forms CN^- ions, which can combine with Fe^{3+} ions present in human organisms and prevent cells from using CO_2 . Moreover, HCN can cause a severe depression of respiratory frequency and then convulsions. Unlike CO, which remains primarily in the blood, CN^- ions are distributed throughout the body and make contact with the cells of tissues and organs. Cyanide ions readily react with the cytochrome oxidase enzyme to form a cytochrome oxidase–cyanide complex, and with methaemoglobin to form cyanomethaemoglobin.⁷¹ A controlled model of the cerebral circulation showed that cyanide and CO act synergistically to reduce cerebral oxygen consumption. A blood CO level of 20% combined with a blood cyanide level of approximately 2 $\mu\text{g/mL}$ can result in death.⁷²

Due to the growing use of nitrogen-containing materials in plastic furnishings, the occurrence of HCN in fires is increasing.⁷³ The potential hazards of this metabolic poison in persons exposed to fire have been found to include elevated blood cyanide levels in air crash casualties.⁷⁴ Some irritant gases are specific to certain types of polymers or additives. Halogenated acids are formed in the gaseous phase by the action of brominated or chlorinated flame retardants, such as polybromodiphenyl ethers (PBDE) or chlorinated paraffins. Elimination reactions involving either PVC or chlorinated elastomers release HCl. Low contents of HCl (100 ppm) can cause severe pulmonary irritations, while high contents (1000 ppm) can cause oedema with lung flooding, even after short exposure times.⁷⁵ The irritant character of some gases is due in particular to partial oxidation of decomposition products of polymers, since aldehydes and ketones are the final products of thermal degradation (thermo-oxidation) of polyolefins. One method for comparing materials according to the amount of toxic gases and irritant production measures the total percent conversion to these species by mass, under standard conditions (e.g. Y_{CO} for yield of CO in units of g/g). The exact yields depend on the O_2 levels, which are determined by the temperature and equivalence ratio.⁷⁶ The production of irritants and toxic gases is also linked to the rate of mass loss. Similar approaches can be used for flame-retarded polymers. Nanoparticles can be integrated into these polymers to serve as flame retardants, taking into account that flame retardants generally increase the percentage conversion to CO, but reduce the rate of mass loss.

The main effects of toxic gas released in a fire, such as incapacitation or death, can be predicted using data about lethality in rats (ISO 13344) or estimates about human toxicity thresholds (ISO 13571). The following equation (N-gas model) from ISO 13344 (equation 2) is based on the concentration for each toxicant corresponding to 50% of the population for a 30 min exposure (LC_{50}). The fractional effective dose (FED), equal to one, indicates that the sum of the concentrations of each compound is lethal for 50% of the population if exposed for 30 min:

$$\text{FED} = m[\text{CO}]/([\text{CO}_2] - b) + (21 - [\text{O}_2])/(21 - \text{LC}_{50, \text{O}_2}) + [\text{HCl}]/\text{LC}_{50, \text{HCl}} + [\text{HBr}]/\text{LC}_{50, \text{HBr}} + \dots \quad [13.2]$$

It must also be noted that post-exposure effects can occur if irritant gases adsorb on submicronic soot particles and possibly on nanoparticles used as fillers or flame-retardant components. These can penetrate deep into the lungs, causing pulmonary irritation. Respiratory distress due to pulmonary oedema may arise from this combined presence of irritant and inflammatory species.

Despite the large amounts of various kinds of particles released by fires, relatively few studies report the role of particles on toxicity, in relation to their intrinsic characteristics (such as composition, structure, size, and surface area). The role of nanoparticles used as fillers, reinforcements or flame-retardant systems components, has only recently been researched in relation to toxicity. Moreover, there are two cases to be distinguished in the combustion of nanocomposites:

- modification of the thermal decomposition pathway of polymer and composite materials (and therefore possible modification of the nature of the gases released) (see section 13.3);
- emission of nanoparticles or additional ultrafine soot particles containing nanoparticles.

Both cases illustrate the interactions between nanoparticles, according to their surface chemistry, size, specific surface area, and the decomposition processes of polymers. However, a key point is to determine if the nanoparticles, released by the combustion processes of nanocomposites, are almost identical to the pristine ones originally incorporated in the polymers. This is important, as the amount of toxicological data about these nano-objects is continuously increasing since the pioneering work of Oberdörster.^{77,78}

13.6 Intrinsic toxicity of nanoparticles

Currently, there are major gaps in our knowledge about the risks posed by nanoparticles. Some of these uncertainties are fundamental and will probably remain for years to come. The effects after long-term exposure to nanoparticles and their bioaccumulation in organisms are particularly challenging issues.

Moreover, uncertainties stem from the wide range of nanoparticles. Their categories (such as silver, titanium dioxide, zinc oxide, carbon nanotubes, and others) are not uniform in terms of size, purity, crystalline form, surface area, porosity and density, and various agents may modify their surfaces in a number of ways. Nanoparticles can be designed to prevent their agglomeration in the matrix structure or to bind them to the matrix, leading to the improvement of nanocomposite properties. Some adaptations aim to modify the physicochemical properties of the nanoparticles. Hence, functionalized nanoparticles may differ greatly from non-functionalized one. Some experts consider modified nanoparticles

13.5 The different anatomical regions of the respiratory tract, from ICRP.⁸¹

as individual substances, e.g. polymer-grafted nano-TiO₂ is considered different from pristine nano-TiO₂.

The potential toxicity of nanoparticles depends on their penetration routes and deposition in the human body. The former can happen by contact, but mainly occurs by inhalation of an aerosol. Deposition in the respiratory tract is a complex phenomenon. It is affected by various anatomical and physiological parameters as well as fluid mechanics, and particle dynamics.⁷⁹ Three anatomical zones can be distinguished (Fig. 13.5), according to the mechanisms of deposition, which are in turn dependent on particle size. These include the extra thoracic (ET, upper respiratory tract), trachea and bronchi (TB), and alveolar (AL) zones.⁸⁰ Table 13.4 presents the exchange surface area between air and human organisms, on which inhaled particles can settle. In the case of a homogeneous deposition, the surface density in the ET zone would be 3000 times higher than in the AL zone.

The deposition of ultrafine particles can occur through the following mechanisms: sedimentation, interception, impaction, diffusion (Brownian motion) or electrostatic interaction. Diffusion is the predominant mechanism for particles smaller than 300 nm. Depending on particle size, the deposition of inhaled particles is not uniform in different zones of the respiratory tract. Figure 13.6⁸² presents both the total fraction and the fractions settled in each zone, for spherical

Table 13.4 Exchange surface area between air and human organism

Main region	Anatomic zone (see Fig. 13.5)	Surface area
Extrathoracic	ET 1	2×10^{-3}
	ET 2	4.5×10^{-3}
Trachea and broncheal	BB (bronchi)	2.9×10^{-3}
	bb (bronchiole)	2.4×10^{-1}
Alveolar	AL	140

13.6 Total fraction and fractions settled in each zone for a person breathing through their nose.⁸¹

particles with a density of 1 g/cm^3 , in a person breathing through their nose. It appears that the maximal fractions for AL (denoted by 'ALV' in Fig. 13.6) and TB zones correspond to the nanometric range.

After penetration and deposition in the AL and TB zones, nanoparticles could cause fluid release and inflammation, preventing oxygen transfer. Inflammation of the terminal bronchioles can result in a complete blockage. Smaller particles may enter the lung interstitium around the pulmonary alveoli close to the blood capillaries, causing interstitial oedema. Nanoparticles can then enter the bloodstream, causing immune responses from the cells.^{83,84}

In this chapter, we have focused on nanoparticles used in polymers for sport equipment, transportation, textiles, and coatings. These nanoparticles are mainly layered silicates, carbon nanotubes, carbon black, nanosilver, and nano-oxides such as TiO_2 , Al_2O_3 , ZnO , and SiO_2 . Although nano- TiO_2 has been studied since the 1980s, present research into nanoparticles risk to the environment and health is mainly concentrated on carbon nanotubes. TiO_2 has widespread applications, for example as a UV absorber, particularly in cosmetics products, and as a photocatalyst. Fine nano- TiO_2 (with a median diameter of about 300 nm, for UV absorption) must be distinguished from ultrafine nano- TiO_2 (median diameter less than 15 nm, for photocatalyst applications). TiO_2 is usually found at the highest concentrations of all nanoparticles in the environment. In treated wastewater, concentrations of 3–16 $\mu\text{g/L}$ can be expected.⁸⁵ *In vivo* investigations on rodents have shown that inhaled nano- TiO_2 may penetrate the air–blood barrier and can be transported by the bloodstream throughout the body. However, the total number of particles transported to the pulmonary epithelium is very low, compared with the initial dose entering.⁸⁶ However, the translocation is increased for ultrafine particles. An inflammatory effect after inhalation of nano- TiO_2 has been observed,

which correlates to the total surface of the nanoparticles and not to mass.⁸³ In addition, the shape of the particle is important, since fibres are more active than more isometric particles.⁸⁷ It has also been observed that the cytotoxicity of anatase was around 100 times higher than that of rutile.⁸⁸

Zinc oxide (ZnO) has similar applications to TiO₂ (UV absorber, photocatalyst). It is easily soluble in water. At high doses, ZnO becomes toxic. Moreover, it has been shown that in combination with solvents (such as pesticides), the translocation of nano-ZnO is increased.⁸⁹ The possible adverse effects of nano-ZnO on lung cells include reduced cell viability, inflammation, and even cell death.⁹⁰ However, particle and Zn ions were not clearly distinguished, since Zn ions at high doses are able to cause cell death.⁹¹ In comparison, Al₂O₃ particles of 20 nm induced an inflammatory reaction in rat lungs.⁸⁹ However, no, or only slight, acute effects were observed in a recent animal study, even after high doses.⁹²

Silver nanoparticles (AgNPs) have antimicrobial properties and are therefore one of the most widely used nanoparticles in commercial products, such as bandages, in textiles and in household products.⁹³ Nevertheless, AgNPs are toxic in living organisms⁹⁴ and chronic exposure to silver is known to cause argyria and/or argyrosis in humans.⁹⁵ Takenaka *et al.* showed that AgNP inhalation can be detected all over the body.⁹⁶ *In vitro* data have shown that nano-Ag may affect mitochondria⁹⁷ and cause DNA damage.⁹⁸ It is not clearly established whether the observed effects are due to free silver ions or to AgNPs. However, Beer *et al.*⁹⁹ have shown that free silver ions in AgNP preparations play a considerable role in the toxicity of AgNP suspensions. Therefore, nano-Ag does have a specific effect, as do other metal-based nanoparticles with relatively high solubility rate, such as CuO nanoparticles.^{98,100}

SiO₂ is either present as various kinds of pure amorphous nanoparticles (pyrogenated, precipitated, colloidal) or is carbon coated (silica fumes). On the whole, *in vivo* studies show that ultrafine particles of amorphous silica lead to strong but non-persistent inflammation effects.^{101,102} Silicotic lesions are confined and partially reversible. Amorphous silica are weakly persistent, since it is partially soluble in organic fluids. However, investigations have shown that silanol content at the surface of silica can affect its cytotoxicity.¹⁰³ Decreasing size entails an increase in cytotoxicity. Conversely, the crystalline form (quartz) leads to progressive but persistent inflammation. Johnston *et al.*¹⁰⁴ showed that chronic inflammatory response, including genotoxic effects in rats, were only observed after inhalation of crystalline nano-SiO₂.

Organomodified montmorillonites and bentonites are the main class of nanoparticles used in polymers. This is due to their reinforcement effects, their permeability to gases and solvent, and their contribution to flame retardancy.^{105,106} They can be seen as an opportunity rather than a risk, since they could remove pollutants from aqueous media, which are trapped inside their interlamellar space. In addition, the nanometric state is obtained after exfoliation or intercalation processes in the host polymers. To date, no studies have investigated the cytotoxicity of montmorillonites alone. Other kinds of lamellar silicates used in polymers as

nanoparticles (such as sepiolite and halloysite) are increasingly used in industry. However, their toxicity has not been established. This issue has rarely been researched with regards to these particles. It has been established that some mineral deposits of these layered silicates can contain a minor fraction of crystalline silica, which can adversely affect the health of workers in mining or the industrial minerals industry.

Carbon-based nanoparticles include carbon nanotubes and carbon black (CB). CBs are powders made of elementary carbon (more than 98 wt%) in primary particles (10 to 500 nm), aggregated (100 to 800 nm), and then agglomerated as micronic particles. Their specific surface area ranges from 10 to 300 m²/g. Hence, these particles are able to penetrate the lung alveoli and a fraction can be considered a nanoparticle. The composition of CBs is significantly different from that of soot, since the composition of the latter can vary and include a high fraction of mineral ashes. CBs have been used for decades in large quantities in products such as tyres and printers, so the toxicological effects on workers are known. Moreover, pure CBs have been used in many studies as a reference nanoparticle to assess the toxicity of other carbon-based nanoparticles. Deposition of CB in the respiratory tract has been recorded and exposed workers have suffered chronic bronchitis and a reduction in respiratory capacity.¹⁰⁷ Fibrotic reaction around CB deposits has also been cited. Studies about pulmonary retention after inhalation have shown that CB behaviour was similar to other particles of low solubility and toxicity. Nevertheless, ultrafine CB (median diameter 14 nm) appears to cause an increased and delayed cytotoxicity compared with fine CB (260 nm).¹⁰⁸ Ultrafine CB therefore entails a higher oxidative stress for cells than fine CB.

Carbon nanotubes are categorized based on their structure (single- or multi-walled, chirality, aspect ratio), process of production (laser ablation, electric arc, catalytic decomposition), and surface modification. The percentage of metallic residual impurities may be high, but a value of less than 1% can be attained using purification steps and depending on the process of production. Consequently, assessment of toxicological risks appears a complex task, given the diversity of these nano-objects.¹⁰⁹

Shvedova *et al.*¹¹⁰ have shown that the introduction of single-wall carbon nanotubes (SWCNT) into human keratinocytes reduces cellular viability. Structural and morphological modifications of the epithelial cells of bronchi occur. Oxidative stress and cytotoxicity can occur, due to the formation of hydroxyl radicals, antioxidant depletion, and finally apoptosis.¹¹¹

Radomski *et al.*¹¹² showed that blood platelet aggregation is influenced by SWCNT and multi-wall carbon nanotubes (MWCNT). Soto *et al.*¹¹³ compared the cytotoxicity of various carbon nanotubes (CNTs) with a primary size in the 3–150 nm range. The authors concluded that the toxicity of CNTs was comparable to that of chrysotile asbestos. Nevertheless, due to the diversity of both CNTs and experimental procedures, studies have reported contradictory results, which generate uncertainty about the potential risk of CNTs. In addition, it has been suggested that most of the toxicological effects observed were due to the presence

of metallic contaminants (Co, Fe, Ni, Mo, Ti).^{114,115} The kind and degree of CNT agglomeration also influences cytotoxicity.¹¹⁶ Functionalization, regardless of the side group, can also have a useful effect, since a change from highly insoluble to water soluble leads to a drastic reduction in toxicity.^{117,118} However, the variety of CNTs does pose problems for understanding their effects and distribution in humans. More reliable assessment of the negative effects of CNTs, with regard to their mechanical, thermal, and electrical properties, is needed due to their increasing use in industrial applications.

Based on investigations of environmental particulate contaminants such as carbon particles, the main biological factors regarding the potential toxic effects of nanoparticles are as follows:

- inflammation
- acute toxicity
- oxidative stress
- DNA damage
- crossing and damage to tissue barriers (e.g. blood–brain barrier, air–blood barrier, and placental barrier).

The potential effects of nanoparticles present in polymer nanocomposites, which can undergo thermal decomposition by incineration or accidental fire, would be significantly different. However, the possible adverse effects will also depend on the nature of the ultrafine particles released (pristine nanoparticles or nanoparticles combined with soot or other ultrafine particles). The circumstances of the fire, the nature of the polymer, and composition of the polymer material mean that the release of nanoparticles into the atmosphere can be significantly different. The next section presents some investigations carried out to assess the potential release of nanoparticles from nanocomposite combustion as well as the morphology and composition of the ultrafine particles released containing nanoparticles.

13.7 Ultrafine particle production during combustion of nanocomposites

The release of free nano-objects in the useful life phase is generally considered negligible because they are strongly embedded in the polymer matrix. In contrast, the waste stage could be a source of free nano-objects; it is highly probable that a substantial fraction of the polymer nanocomposites will ultimately be incinerated, due to the lack of suitable waste collection for many products. Hence, it is essential to avoid emission of free nano-objects. Currently, most waste incinerators are not able to completely remove the nano-objects from the gases released. According to Zeuthen *et al.*,¹¹⁹ a significant fraction (around 20%) of particles smaller than 100 nm are not captured by electrostatic precipitators, fabric filters or wet scrubbers. Roes *et al.* recently evaluated the number of nanoparticles released by incinerators from waste containing nanoparticles.¹²⁰ The number of nano-objects in an average

waste sample is calculated according to the assumptions that nanoparticle content in nanocomposites is 1 wt% (low estimate) or 10 wt% (high estimate) and average municipal solid waste contains 12% plastics.¹²² In 2020, the share of nanocomposites among plastics in the USA is estimated to reach 7%.¹²² In most cases, the extra nano-objects in the released gases are estimated to be 100 to 10000 times higher than in conventional waste, assuming that nanoparticles are not destroyed.

The nanoparticles can then be destroyed, modified or released. They can be destroyed by combustion (organic particles), oxidation or reaction with strong acids, modified by chemical reactions into secondary nanoparticles, or released with fly ashes. The effect of the incineration process and the temperature range inside the incinerator differ according to the nanoparticles present in the nanocomposites. Some nano-oxides such as TiO_2 and silica are thermally stable up to 1200 °C, which is roughly the maximum temperature in an incinerator. In contrast, other types of nano-oxides can react with acid gases generated from the thermal degradation of various materials. For example, ZnO can form ZnS or ZnSO_4 depending on the reducing or oxidizing conditions. ZnCl_2 can also form due to HCl release. Similarly, AgNP can form AgO, by oxidation, or form a secondary NP, AgCl. In the presence of phosphorous species, alumina-based nanoparticles can form stable AlPO_4 . In oxidizing conditions, aluminium sulphate particles can also be formed.

Carbon-based nanoparticles would be destroyed by combustion. Nevertheless, as mentioned in section 13.3, carbon nanotubes can build a thermal shield at the surface of the residual material and can therefore remain intact inside this shield.²⁶ Furthermore, unreacted carbon black might be released with the fly ash.

More complex situations could arise because metals released during the incineration process might condense at the surface of non-toxic nanoparticles, leading to a marked increase in toxicity. Experimental work has been carried out using specific furnaces or cone calorimeters coupled with impactors to analyse the morphology and composition of the resulting nanoparticles.

Fire retardants containing polyamide-6 (PA-6) and polypropylene (PP), nanofillers or a combination of both flame retardants have been investigated using the steady-state tube furnace (ISO/TS 19700) by Stec *et al.*^{123,124} The samples were tested under three different fire conditions ($\Phi < 1$ fuel lean flames, $\Phi = 1$ stoichiometric flames, $\Phi > 1$ fuel rich flames), to assess the influence of additives on the soot production or toxic product yield.

The fire-retardant additive used for polypropylene was ammonium polyphosphate (APP) and the nanoparticles were modified montmorillonites (OMMT) using a suitable organomodifier (Cloisite 20A). For PA-6, a mixture of aluminium phosphinate and melamine phosphate was used (OP 1311, Clariant), combined with a different OMMT (Cloisite 30B) suitable for PA-6. The amount of flame retardant was 30 and 18 wt% in polypropylene and PA-6 respectively, while the OMMT content was limited to 5%. The total soot yield was very similar for most of the samples under most fire conditions. However, flame retardant/OMMT combinations increased the amount of soot, mainly for particles between 0.5 and 1.0 μm , for each

fire condition. Particles smaller than 0.5 μm contributed significantly to soot production, but the size distribution of particles was not influenced by the ventilation conditions. For larger particles in under-ventilated conditions, the largest mass was around 0.93–1.55 μm diameter for polypropylene containing flame retardant or flame retardant/OMMT. The research concluded that only the incorporated additives and not the polymer would determine the soot particle size.

Motzkus *et al.*⁷ studied the combustion behaviour and the characterization of solid and gaseous fire effluents of polymers (polymethylmethacrylate (PMMA) and polyamide-6 (PA-6)) filled with silica, alumina, and CNT nanoparticles. They aimed to determine the impact of these compositions on the emission of airborne particles produced for various fire scenarios. The experimental setup combined a cone calorimeter and a low-pressure impactor with a condensation nuclei counter (see section 13.4.2) to determine the particle size distribution in the 30 nm to 10 μm range, and the concentrations of submicronic particles in the aerosol corresponding to the smoke.

Pristine polymers and polymers with nanoparticles were compared. The influence of nanoparticle surface treatments (silane-based) and combinations with APP, to improve fire retardancy, were investigated. For all formulations of PMMA or PA-6, with and without nanoparticles, the results illustrated that high mass fractions were obtained for the submicronic particles (close to 80%). The presence of nano-oxides in PMMA had a significant effect on the rate of particle emission, decreasing the concentration of the emitted submicronic particles.

APP in PMMA led to a decrease in the mass fraction of ultrafine particles and an increase in the rate of submicronic particle emission, compared with compositions filled with nano-oxides. In the case of PA-6, there was a slight decrease in the mass fraction of submicronic particles and of ultrafine particles for the APP with SiO_2 . In addition, the results suggest that the silane surface treatment of nanoparticles incorporated in PMMA could decrease the concentration of submicronic particles.

Atomic force microscopy was used as a complementary tool for measuring the ultrafine particles released during combustion. This allowed direct observation of nanoparticle morphology, detection of carbon nanotubes in the aerosol, and visualization of the effect of APP on nanoparticle morphology. Figure 13.7 presents some of the most representative AFM images of the particles collected on the first stage of the impactor corresponding to a cut-off aerodynamic diameter of 30 nm for different compositions. Only phase images are presented, since they have a stronger contrast, rendering image interpretation easier. Particle sizes were evaluated directly from measuring the topography images.

A complementary study, focusing on the behaviour of CNT, was carried out by Asharani *et al.*⁶⁵ The results mainly show that the addition of MWCNT leads to a significant decrease in the peak heat release rate measured using a cone calorimeter. This effect depends on the matrix and shows a different mass ratio for carbon nanotubes. There was no significant difference in the mass size distribution of aerosols between PA-6 and the corresponding PA-6/MWCNT nanocomposites.

13.7 Particle sizes evaluated directly from dimensional measurement by atomic force microscopy (AFM).⁷

The incorporation of MWCNT into PMMA seems to reduce the proportion of larger particles emitted, within the 0.6–2.5 μm range. Conversely, the particle size distribution for the PMMA with MWCNT shows an increase in particles larger than 4 μm , corresponding to the last three size classes of the impactor, compared with PMMA alone. Carbon nanotubes have been observed using AFM for a cut-off diameter of only 30 nm for PA-6/MWCNT (Fig. 13.7).

13.8 Conclusion and future trends

Polymer nanocomposites and engineered nanoparticles are expected to hold considerable potential for products that offer improved or novel functionalities. Nanotechnologies could open the way for the use of new applications in materials, but also in the environment and in health, for example using original surface

modifications of nanoparticles incorporated in polymers. However, the unintentional release of engineered nanomaterials from these products can affect the environment and human health. The product life cycle and particularly the end of the product's usage determine the various environmental and health exposure situations. Accidental thermal degradation by exposure to a heat source or a fire and combustion of nanocomposites in incinerators can cause emission of ultrafine particles and nanoparticles. Limited information about toxicological effects is available although further research is in progress for many types of pristine nanoparticles and some surface-modified ones. Information is lacking about the potential risks associated with the thermal and combustion decomposition products of nanocomposites.

Various studies have highlighted that the incorporation of nanoparticles in polymers can increase thermal stability and act as a fire retardant. But few works have studied the interactions between gaseous degradation products and nanoparticles, potentially leading to a modification of the degradation pathway of polymers. Only organomodified montmorillonites and nano-oxides can cause significant catalytic activity, allowing the nature of the evolved gases to be modified. In addition, further research is needed into the composition and morphology of ultrafine or secondary nanoparticles released during combustion of nanocomposites.

The objective of the Nanofeu and Innanodep projects is to fill this gap by experimenting under various fire scenarios using original combinations of cone calorimeter, low-pressure impactor, and characterization devices, such as an FTIR and condensation nuclei counter. The results obtained so far in the Nanofeu project show that the presence of nanoparticles (nano-oxides) in PMMA entails, paradoxically, a decrease in the concentration (particles/cm³) of the emitted submicronic particles, in comparison with pure polymer. Moreover, a silane surface treatment of nanoparticles seems to cause a further decrease in the concentration of submicronic particles. The combination of nano-oxides with a flame retardant (ammonium polyphosphate) causes a pronounced increase in the concentration of cohesive residue at the surface of the remaining material.

The mechanisms of combinations of nanoparticles, possibly modified by the combustion atmosphere (oxidation, reaction with acids) with soot or other ultrafine particles during thermal degradation need to be investigated for various scenarios and types of nanocomposites. Their entry and deposition in the respiratory tract could have direct effects on human health. Further investigations carried out in the Innanodep project using atomic force microscopy, electron microscopy, and energy-dispersive X-ray spectrometry, will help extend our knowledge about morphology and composition of the released nano-objects and ultrafine particles.

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