Explosion risks from nanomaterials

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Explosion risks from nanomaterials

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Abstract. Emerging nanomanufactured products are being incorporated in a variety of consumer products ranging from closer body contact products (*i.e.* cosmetics, sunscreens, toothpastes, pharmaceuticals, clothing) to more remote body-contact products (electronics, plastics, tires, automotive and aeronautical), hence posing potential health and environmental risks. The new field of nanosafety has emerged and needs to be explored now rather than after problems becomes so ubiquitous and difficult to treat that their trend become irreversible. Such endeavour necessitates a transdisciplinary approach.
A commonly forgotten and/or misunderstood risk is that of explosion/detonation of nanopowders, due to their high specific active surface areas. Such risk is emphasized and illustrated with the present development of an appropriate risk analysis. For this particular risk, a review of characterization methods and their limitations with regard to nanopowders is presented and illustrated for a few organic and metallic nanopowders.

1. Introduction

For the past 10 years, there has been a growing interest in developing nanomaterials in various industrial sectors such as catalysts, in cosmetics, paints and coatings, because of their unique properties. Some of these materials that have traditionally been manufactured are now being developed as new products on the nanoscale. Others show truly new structures, such as carbon nanotubes. Concerning carbon nanotubes (CNTs), their market is positioned to "grow explosively" to reach 540 millions of dollars per year in 2007-2008 and more specifically 340 millions of dollars per year, for multi-walled carbon nanotubes (MWNT) [1]. CNTs production is going to increase in the coming years and consequently potential risks associated to the handling of CNTs will be proportionally more and more important.

Aluminium powders have long been employed as fuel ingredients, explosives, propellants to enhance energy density and stability of propulsion systems. Aluminium is added to improve the burn rate and enhance blast effects in explosives [2, 3].

For any powders set in suspension in air, the ease with which they ignite, burn and propagate varies considerably with important factors that have to be characterized so as to be able to control their explosion. One of them is obviously the particle size, which takes nanopowders now under higher scrutiny for OH&S issues, others are the particle concentration, the degree of de-agglomeration, and the degree of turbulence [4, 5]. So far, literature studies concerning the evaluation of explosion and flammability hazards of powders were essentially carried out on microsized powders, including one on

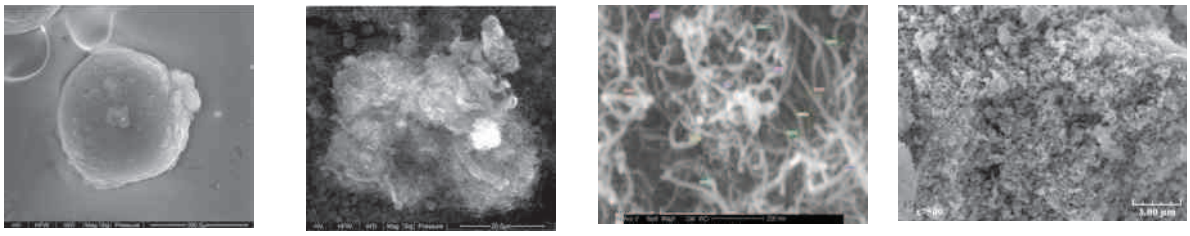
nanomaterials explosivity published in 2004 [6]. This work proposes to review recently measured main explosion safety parameters of multi-walled carbon nanotubes, carbon blacks and aluminium nanoparticles performed in course of the EU Nanosafe2 project.

2. Experimental setups and methods:

2.1. Particle geometrical characteristics

In this study, multi-walled carbon nanotubes were provided by an industrial partner of the Nanosafe2 consortium. Some geometrical characteristics were unknown and were determined during this work. The particle-size distribution, determined by using a laser diffraction analyzer (Mastersizer, Malvern Instrument) and performed in isopropanol, was characterized by the d_{10}, d_{50} and d_{90} of the volumetric distribution. The d_{10}, d_{50} and d_{90} values (*i.e.* particle size at 10%, 50, and 90% of the cumulative particle size distribution) are respectively 20, 200 and 560µm.

It has to be noticed that carbon nanotubes seem to form large agglomerates, which is confirmed by the transmission electronic microscope analysis.



A B C D

Figure 1. TEM images of the MWNTs carbon nanotubes (A-C) and aluminium nanoparticles (D) at different resolutions

TEM observations of CNTs shows particles appearing as large spheres with imbedded nanotube networks having a diameter ranging between 15 and 20 nm.

Similar investigations were carried out with three nano-sized aluminium powders supplied by industrial partners of the consortium. Their surface is covered with an alumina layer representing approximately 20-30% by weight.

BET specific surface areas (S_{BET}) and helium pycnometer density have been measured. By coupling the results obtained by BET and helium pycnometer, an average grain size can be calculated by considering that particles are isolated, cylindrical (or) spherical with a monodispersed size distribution:

$$d_{BET} = \frac{4(or)6}{\rho_{helium} \cdot S_{BET}} \qquad (1)$$

2.2. Sample preparation for safety parameter characterisation:

A good reproducibility between the different tests was ensured by systematically drying the samples at 50°C under dynamic vacuum of 1 Pa during 15 minutes and then under a static vacuum of 10 Pa during 4 hours before handling. Particular attention was taken to handle the nanopowders. Nitrile gloves, airline hood, non-woven coverall and HEPA/ULPA vacuum cleaner have been used in addition to the more classical safety barriers.

2.3. Explosion sensitivity and severity

Explosion sensitivity is often referred to as a combination of three parameters characterizing the ability of dust to be ignited and to generate dust explosions. These parameters are the following: the minimum ignition energy (MIE), the minimum ignition temperature (MIT) and the minimum explosive concentration (MEC) [7, 8].

In our study, MIE was determined using a modified Hartmann tube (Kühner AG). It consists in a 1.2 L glass cylindrical vessel in which the powders are dispersed and ignited by an electric spark. Both spark's energy and dust concentration could be modified to characterize the MIE. Turbulence degree is also variable. This apparatus also allows the determination of the MEC [9].

MIT in cloud can be tested by using a Godbert-Greenwald furnace (Chilworth Technology) set in an unconfined environment. This parameter was not systematically measured in our study.

The measurements of dust explosion severity, *i.e.* P_{max} (maximum overpressure), and $(dP/dt)_{max}$, (maximum rate of pressure rise), were performed in a 20 L spherical vessel in accordance with the ASTM Method E 1226 (see Figure 3). Explosion severity is quantified by an explosion index K_{st} which is defined as

$$K_{st} = \left(\frac{dP}{dt}\right)_{\max} \cdot V^{1/3} \qquad (2)$$

where V is the explosion volume.

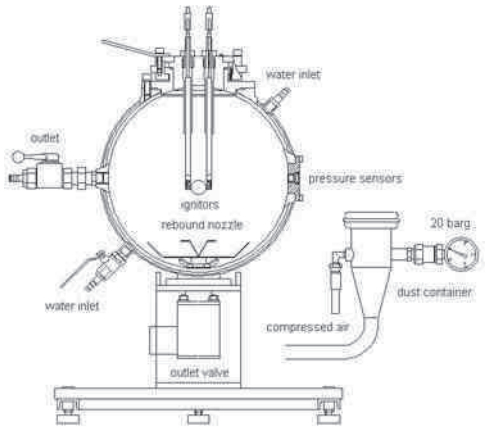


Figure 2. Schematic representation of the 20 L apparatus (Kühner AG).

3. Results and Conclusions

The main results of this study are summarized in the following Table 1.

Table 1. Main safety parameters for CNTs, Carbon blacks and Aluminium

Products	CNT	Carbon blacks				Aluminum		
		Corax N115	Corax N550	Thermal Black N990	Printex XE2	Alex	100 nm	200 nm
MIE (mJ)	> 1J	> 1J	> 1J	> 1J	> 1J	<8mJ	< 1mJ	7 mJ
MEC (g/m3)	45	60	60	60	60	60	-	-
Pmax (bars)	6,6	7,7	7,5	6,7	7,2	8.3	8.2	9.5
(dP/dt)max (bars/s)	227	326	503	240	343	933	1340	2480
Kst	62	88	136	65	93	253	365	675
Explosivity Class	St1	St1	St1	St1	St1	St2	St3	St3
S_{BET} (m^2/g)	195	128	42	9	900	-	23	10.5
d_{BET} (nm)	10	23	70	330	3	-	100	200
d_{agg} (nm)	200 000	90 000	15 000	2000	88000	~80000		

From this table, it is shown that although the primary particles are estimated by the BET method, the resulting average particle diameter (of the order of 10-200 μm) is much larger than the particle primary size indicating that the particles are agglomerated.

The maximum explosion pressure for the studied carbon blacks is 6.6 bars which is slightly lower than the value for MWNTs. The maximum rate of pressure rise is 227 bar/s and the explosion index K_{st} is 62, lower that that of carbon blacks, ranking the explosivity of these powders in a low hazard

range. It is seen, however, that for aluminium nanopowders, the explosion sensitivity is high and that the severity can also be very high (K_{st} of 675), greater than that of hydrogen which is considered as a detonable gas. Hence, metallic nanopowders can possibly detonate under certain conditions, thus providing grounds for the need to perform a thorough risk assessment for such types of nanopowders.

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