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Preliminary evaluation of risks related to waste incineration of polymer nanocomposites

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ABSTRACT

If nanotechnology proves to be successful for bulk applications, large quantities of nanocomposites are likely to end up in municipal solid waste incineration (MSWI) plants. Various studies indicate that nanoobjects might be harmful to human health and the environment. At this moment there is no evidence that all nanoobjects are safely removed from the off-gas when incinerating nanocomposites in MSWI plants. This paper presents a preliminary assessment of the fate of nanoobjects during waste incineration and the ability of MSWI plants to remove them. It appears that nanoobject emission levels will increase if bulk quantities of nanocomposites end up in municipal solid waste. Many primary and secondary nanoobjects arise from the incineration of nanocomposites and removal seems insufficient for objects that are smaller than 100 nm. For the nanoobjects studied in this paper, risks occur for aluminum oxide, calcium carbonate, magnesium hydroxide, POSS, silica, titanium oxide, zinc oxide, zirconia, mica, montmorillonite, talc, cobalt, gold, silver, carbon black and fullerenes. Since this conclusion is based on a desktop study without accompanying experiments, further research is required to reveal which nanoobjects will actually be emitted to the environment and to determine their toxicity to human health.

1. Introduction

The use of reinforcing additives in polymers is a widely known technology that has been applied for decades. Reinforcing additives are materials, which, when embedded in a polymer matrix, result in an increase in the tensile strength and the tensile modulus of elasticity of the composite compared to the neat matrix. Very common reinforcing additives in the micrometer scale have been glass fibers, carbon fibers, organic aramid fibers and natural wood fibers (Erhard, 2006).

A new type of materials for the reinforcement of polymers involves nanoobjects. Nanoobjects are objects that have at least one dimension in the order of 1–100 nm (1 nm $= 10^{-9}$ m), comprising nanoparticles that are nanoscale at three external dimensions, nanofibers that are nanoscale in two external dimensions and nanoplates that are nanoscale on one external dimension (International Standards Organisation, 2008).

The use of nanoobjects for reinforcement of polymers has raised high expectations since it has shown to improve the mechanical properties significantly. Furthermore, it has been shown that the use of nanoobjects as reinforcing additive can have potential benefits also from an environmental point of view (Roes et al., 2010). It is therefore expected that, when the technology has matured, it will be applied on a large scale in the near future and 'polymer nanocomposites' will be produced in bulk quantities.

Nanoobjects that are incorporated in polymer nanocomposites might pose a severe risk to human health, if they are released to the environment as free nanoobjects. As we will discuss in this article, there are indications that free nanoobjects change physiological mechanisms and may hence have negative impacts on human health and the environment (Section 3). Given this situation, the precautionary principle requires that measures are taken to avoid the release of free nanoobjects.

Although it may require challenging technical measures (CEA, 2010; FIOH, 2010), it is likely that the release of nanoobjects during the *production process* can be avoided to a large extent. Similarly, we expect that the release of free nanoobjects in the *use phase* is of minor importance because they can be assumed to be firmly embedded in the polymer matrix (exceptions may be products which are subject to abrasion or used under chemically harsh conditions). In contrast, the waste stage could be a potential source of free nanoobjects.[1] Since it is very probable that a substantial share of the polymer nanocomposites will ultimately

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[1] An additional risk might be the collection of the waste. If this occurs with compacting trucks, there is a risk of abrasion and, hence, a release of nanoobjects. This will not be treated in this study, but is recommended for further research.

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be incinerated once their useful life has come to an end, it is essential that the emission of free nanoobjects is avoided.[2]

At this moment, it is not fully clear whether waste incinerators have the ability to completely remove the nanoobjects from the off-gasses, thus avoiding nanoobject emissions to the environment. The aim of this study therefore is to conduct a first prospective review of possible risks of free nanoobjects as a result of incomplete removal by municipal solid waste incineration (MSWI) plants.

In Section 2, the approach of this study is explained. In Section 3, a short review of the toxicology of nanoparticles is given. Section 4 deals with municipal solid waste incineration and processes that determine the fate of nanoobjects. In Section 5, the results of the preliminary risk assessment are outlined. Section 6 is the discussion and Section 7 summarizes the most important conclusions and directions for further research.

2. Approach

In order to identify possible risks of nanoobject emissions after municipal solid waste incineration, the waste incineration process is studied and discussed in this paper. Information on the processes was obtained by means of a literature survey and from the municipal solid waste incineration plant in Amsterdam, Netherlands ('Afval Energie Bedrijf — AEB'). We focus on the processes that are responsible for the fate of nanoobjects. This could be e.g. destruction or conversion in the incineration stage or possible removal during off-gas treatment. For each of these processes, the conditions that determine the fate of the nanoobjects are identified. A decision tree is constructed that provides a general methodology for the risk assessment of nanoobjects when they are incinerated in a municipal solid waste incineration plant.

As a next step, information was gathered on a subset of nanoobjects, involving data on chemical composition and size. These are important factors that determine the fate of the nanoobject during the treatment in a MSWI facility. For example, the size of the nanoobjects determines whether or not they are removed by off-gas filters, whereas the chemical composition determines whether or not the nanoobject is oxidized or undergoes other chemical reactions, or whether it remains inert. Using the decision tree it is determined which nanoobjects possibly leave the grate incineration process and to what extent they are removed in the off-gas treatment section (with high or low efficiency). In this way, possible risks of nanoobject emissions are identified.

It should be noted that the analysis in this study is a preliminary risk assessment, which should formulate first warnings and suggestions for further research. The study was desktop-based, and no experiments have been carried out.

Before the analysis on the waste incineration process, we give a short review on the toxicity of nanoobjects in Section 3.

3. Toxicity of free nanoobjects

The main purpose of this section is to provide an overview of the possible health risks of free nanoobjects. It does not claim to be a complete literature review of the published studies on health risks of nanoobjects, but it indicates which toxic effects have been shown to be related to exposure to nanoobjects. For a more extensive review, we refer to Savolainen et al. (2010).

In our daily lives, we are surrounded by nanoobjects. A normal room can contain 10,000 to 20,000 nanoobjects per cm^3. In a forest, this can be 50,000 nanoobjects per cm^3 and in urban streets it can even be 100,000 nanoobjects per cm^3. These levels are not necessarily harmful (Gezondheidsraad, 2006; Lauterwasser, 2005). However, exposure levels and risks might increase especially in the vicinity of MSWI plants, when nanocomposites are produced in bulk quantities and if harmful nanoobjects are not removed during waste management.

The risks that nanoobjects represent for human health are determined by their toxicity, persistence in the environment, and bioaccumulation. In general, humans can take up nanoobjects by means of inhalation, ingestion, or, in some cases, absorption through the skin. When nanoobjects are inhaled, they can affect the human body in two major ways (Lauterwasser, 2005; Oberdörster et al., 2005; USEPA, 2007):

- they can induce inflammation of the respiratory tract and cause tissue damage and subsequent systemic effects or
- they can be transported through the bloodstream to other vital organs or tissues in the body where they may cause cardiovascular and extrapulmonary complications.

Normally, uptake via the skin rarely occurs although the risk may be higher for individuals whose skin is damaged by, for example, the sun or eczema. Penetration through the skin can lead to cell damage, since nanoobjects can facilitate the production of reactive molecules. The composition, size, and surface characteristics of the nanoobjects determine their distribution in the body. Durable, biopersistent nanoobjects may accumulate in the body, in particular in the lungs, brain, and liver.

It has been shown that the presence of nanosized ceramic and metallic particles is likely to modify the function of human macrophages (Lucarelli et al., 2004). This is a crucial result because macrophages represent the first line of the immune defense: they attack intruders and cause inflammation (M1 type) and they have an important role in vascular repair (M2 type). A good balance between these two functions is important in order to avoid the risk of deficiency to attack intruders on the one hand and the risk of continuous inflammation on the other. Lucarelli et al. (2004) conducted in vitro experiments with naïve macrophages, i.e. macrophages that have not yet reached the development stage M1 or M2. They found that SiO_2 nanoobjects strongly biased naïve macrophages towards inflammation (M1 polarization) and that also cobalt (Co) nanoobjects promote inflammatory mechanisms. Conversely, ceramic nanoobjects of titanium and zirconium were found to have an overall anti-inflammatory effect.

It has also been shown by Muller et al. (2005), Jia et al. (2005) and Poland et al. (2008) that carbon nanotubes exhibit great respiratory toxicity. Muller et al. showed that carbon nanotubes persist in rat lungs, induce an inflammatory response and induce lung fibrosis. Jia et al. showed that carbon nanotubes damage alveolar macrophages, which are responsible for the removal of (possibly toxic) particles that are inhaled with air. Poland et al. showed that carbon nanotubes in fact show a pathogenicity that is similar to that of asbestos.

MohanKumar et al. (2008) studied the influence of fine and ultrafine particulate matter (PM) on the brain and nervous system. They found that PM exposure induces inflammation reactions in the brain and, as a result, an increase of the stress hormone cortisol. PM can also reduce the cellular energy of cells and cause depolarization of the mitochondrial membrane, which marks the opening of the permeability transition pore. This is the beginning of apoptosis (i.e. 'programmed cell death'). By entering cells, PM can damage DNA. It was found, that most prominent genes affected by PM were related to inflammatory processes of the brain and were associated with signaling of innate immune markers.

Nanoobjects have also been shown to exhibit ecotoxicity. For example, Lin and Xing (2007) and Doshi et al. (2008) showed that exogenous nanoobjects, containing zinc and aluminum, exert toxic effects on germination and growth of roots in the seedlings of six agriculturally relevant plant species. Baun et al. (2008) indicated the toxicity of C_{60}, carbon nanotubes and titanium dioxide to an aquatic invertebrate, *Daphnia magna*. Furthermore, titanium dioxide nanoobjects exert genotoxic and cytotoxic effects on fish cells (Vevers and Jha, 2008; Handy et al., 2008).

[2] When polymer nanocomposites are recycled, polymers containing nanoobjects might be mixed with virgin polymers. In such case, also the incineration of conventional polymers could entail a risk.