SAFE USE OF NANOMATERIALS IN POLYMER COMPOUNDS - EXTRUSION AND INJECTION MOULDING

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2. Organisations involved

Zentrum für BrennstoffzellenTechnik GmbH, Duisburg

3. Description of the case

3.1. Introduction

The Zentrum für BrennstoffzellenTechnik (ZBT) is specialized among others on supplying the fuel cell industry with bipolar plates made from polymer compounds. The bipolar plate materials are extruded and processed in traditional production sites using regular extrusion and processing equipment.

The use of carbon nano tubes (CNT) was planned in order to enhance the polymer compounds' performance. The production would involve the compounding of polymers, graphite and carbon nano tubes via extrusion, the injection moulding and the mechanical processing of the bipolar plates.

As theoretically at any of the workplaces in the production line could give rise to exposures, ZBT analysed its extruder and injection moulding equipment with regard to their adequacy for managing potential risks from the use of CNTs.

The development of fuel cells using bipolar plates made from nano-enhanced composite materials was part of a large scale research project (SAPHIR[1]) in the 6th EU Framework Programme for Research and Development and ended in September 2010. The general objective of this project was

[1] The project dealt with the **sa**fe, integrated & controlled **p**roduction of **hi**gh-tech multifunctional materials and their **r**ecycling; http://www.saphir-project.eu/index.php?id=41

the safe, integrated and controlled production of multifunctional nanostructured products including their recycling and ensuring competitive production technologies. The risk assessment work was an integral part of the project for all workplaces of the cooperation partners. Also in further research projects initiated by the German Inno.CNT-Alliance[2] funded by the German Federal Ministry of Education and Research the topic of CNTs for bipolar plates is currently subject of investigation and testing at ZBT.

ZBT compiled and analysed all literature and information from the supplier on the toxicological properties of the used particles. Concluding from that and pursuing the precautionary principle, measures to reduce exposures were foreseen in the set-up and the implementation of new processing equipment, such as glove boxes and air exhaust systems, depending on the type of workplace and the activity carried out (e.g. open use of dusty materials, processing of granulates). Furthermore, the workers use personal protective equipment (gloves, respirators and protective overalls). The effectiveness of these measures was assessed by different qualitative and quantitative approaches.

3.2. Aims

The project aimed at preventing any potential risks for workers from the use of CNTs. It wished to assess and implement the highest level of protection possible and to thoroughly inform all workers of these risks.

3.3. What was done, and how?

In the context of ZBT's research and development work on enhanced material properties of polymer compounds, the use of carbon nano tubes (CNT) was envisaged to produce a novel composite material. It was an important part of the research project SAPHIR[1] as well as an essential objective of ZBT's policy to ensure that due to the introduction of the new material – CNT – no risks to workers could occur.

ZBT was confronted for the first time with the following questions:

- What must be done in order to safely handle CNTs / nanoparticles?
- Which steps should be implemented to minimise potential exposures?
- Which methods exist to analyse exposures and are they sufficient?
- Which technical measures should be implemented and which types of personal protective equipment should be used?
- How can workers and customers be informed about appropriate measures for safe handling and use of CNTs?

The work process was oriented among others to the guide for activities using nano materials published by the German Federal Institute for Occupational Health and Safety[3].

3.3.1. Assessment of information: analysis of the future product

As first step ZBT identified the hazards connected to the use of the new product.

The supplier of the CNTs comprehensively informed ZBT about which potential properties of the substance might harm human health. ZBT analysed the safety data sheet and obtained additional information from the supplier directly. This information included the supplier's evaluation of available literature and different tests with the material he had conducted, in particular with relevance to workers' protection issues.

[2] www.inno-cnt.de
[3] Bundesanstalt für Arbeitsschutz und Arbeitsmedizin: Leitfaden für Tätigkeiten mit Nanomaterialien am Arbeitsplatz, Berlin/Dortmund/Frankfurt, im August 2007, only available in German

The CNTs used by ZBT belong to the group of short, thin and coiled multi-walled CNTs. For this group of CNTs the supplier's could only identify very few studies. Of the studies that were found, there were none, which indicate that this type of CNTs could cause fibre-specific effects after short term exposure (acute tests) or could be related to cancerogenic effects (long-term testing). Some of the studies on short, thin and coiled multi-walled CNTs do indicate effects but it is not possible to deduce a specific and consistent mode of action. Due to this and because the CNTs tested in the published studies were not identical with those of the supplier, the supplier decided to carry out tests himself.

The test results with the site-specific material showed:

- No acute oral toxicity (rat)
- No acute dermal toxicity (rat)
- Inhalation toxicity, acute: inflammatory reaction of the lung at high exposure concentrations, lung toxicity (rat) at 241 mg/m^3
- Inhalation toxicity, sub-acute, sub-chronic and long term: at concentrations above 0.1 mg/m^3 effects[4] were observed in rats
- Not irritating to skin or eyes
- No sensibilisation of the skin
- No damaging effects to chromosomes and no gene mutation observed in vitro

Based on the information on the inhalation toxicity the manufacturer of the CNTs derived and recommended an occupational exposure limit value. The lowest exposure concentration at which no effect was observed in animal testing (NOAEL) was used for this. The value of 0.1 mg/m^3 was multiplied with a safety factor of 0.5 and an OEL of 0.05 mg/m^3 derived.

3.3.2. Assessment of information: analysis of activities

Having identified a potential hazard via inhalation of CNTs, ZBT started a second step in the risk assessment and analysed the production process in order to identify potential sources of exposure. The analysis of activities was done according to BAuA's flow diagram of the guide for safe handling of nanomaterials at the workplace. The following activities were identified as relevant in the 'old' processing equipment:

- Filling of CNTs into the extruder
  In the 'old' installation, all raw materials were handled openly and manually filled into the extruder. The workers used respirators, gloves and protective clothes
- Extrusion of the compound to produce granulates
  The extrusion of polymer compounds was conducted at temperatures between 150 and 280 °C. The exposure to volatile substances, which could potentially be released from the polymer compounds were controlled using several local exhaust ventilations, which were connected to a washer. In addition, a hall ventilation with high air exchange rates existed. The concentrations of emitted substances are normally quite low and the hazard profile of the substances used in the old installation is low.
- Re-melting of granulated and injection moulding process
  The injection of the re-melted compound was conducted as open process in the conventional, old installation with a pointed local exhaust ventilation, because it is assumed that the components are included in the polymer matrices[5].

[4] Observation of pulmonary and extra-pulmonary disposition, BAL and histopathology. The effects were stated to depend on 'overload effects', which means that they are among other likely to be conditioned by the fact that the lung is not cleaned completely anymore and does therefore not sufficiently function.

[5] The assumption that CNTs may or may not be released was checked by measurements with the CNTs

- Manual processing of bipolar plates (milling, drilling, sawing etc.)
  In mechanical processing steps, the bipolar plates can break or chips could be separated from the main material[5].

3.3.3. Assessment of information: the supplier's exposure assessment

In order to get a feeling for potential exposure levels, ZBT obtained respective information from the supplier: The manufacturer of the CNTs had conducted exposure measurements at his (closed) extruder. He had not detected any particles in workplace air during his assessment.[6] The supplier had also predicted that relevant exposures could be excluded for the use phase of the CNTs because they would be integrated in the polymer matrix.

3.3.4. Assessment of information: safety advice of the supplier

Knowing of potential exposures of workers to the CNTs, the Zentrum für BrennstoffzellenTechnik made itself aware of the safety advice of the supplier in order to check, if the implemented risk management measures correspond to the supplier's recommendations.

In the supplier's safety data sheet it is recommended to ensure safe handling and use of CNTs by implementing protection measures. It is particularly advised to minimise the formation of dusts and to ensure sufficient air exchange rates, as well as to extract dusts from the workplace by exhaust ventilation systems. A possible danger of explosion is also indicated. In case CNTs are handled in activities that give rise to dusting, the use of respirators (filter type P2) as well as gloves, goggles and protective clothes is advised. If direct contact with the product is possible, a chemical-safe overall is recommended.

3.3.5. Risk assessment

After all information on hazards of the CNTs, the processes at the workplaces and the potential sources of exposures had been collected, ZBT used it to perform a qualitative risk assessment, assuming the CNTs were used in the process.

ZBT's qualitative risk assessment at the workplaces was hence based on the supplier's information in the safety data sheet and the analysis of activities as well as the implemented protection measures. The analysis focused on potential inhalative exposures of workers, because indications of respective hazards had been found. Furthermore, it was in the interest of ZBT to reduce any potential exposure as much as possible and to thereby use all options to prevent risks.

The risk assessment and analysis of protection measures in the 'old' production line revealed potential risks at all processing steps and at all work places. The following figure summarises this work step.

[6] Detection limit: 5µg/m^3

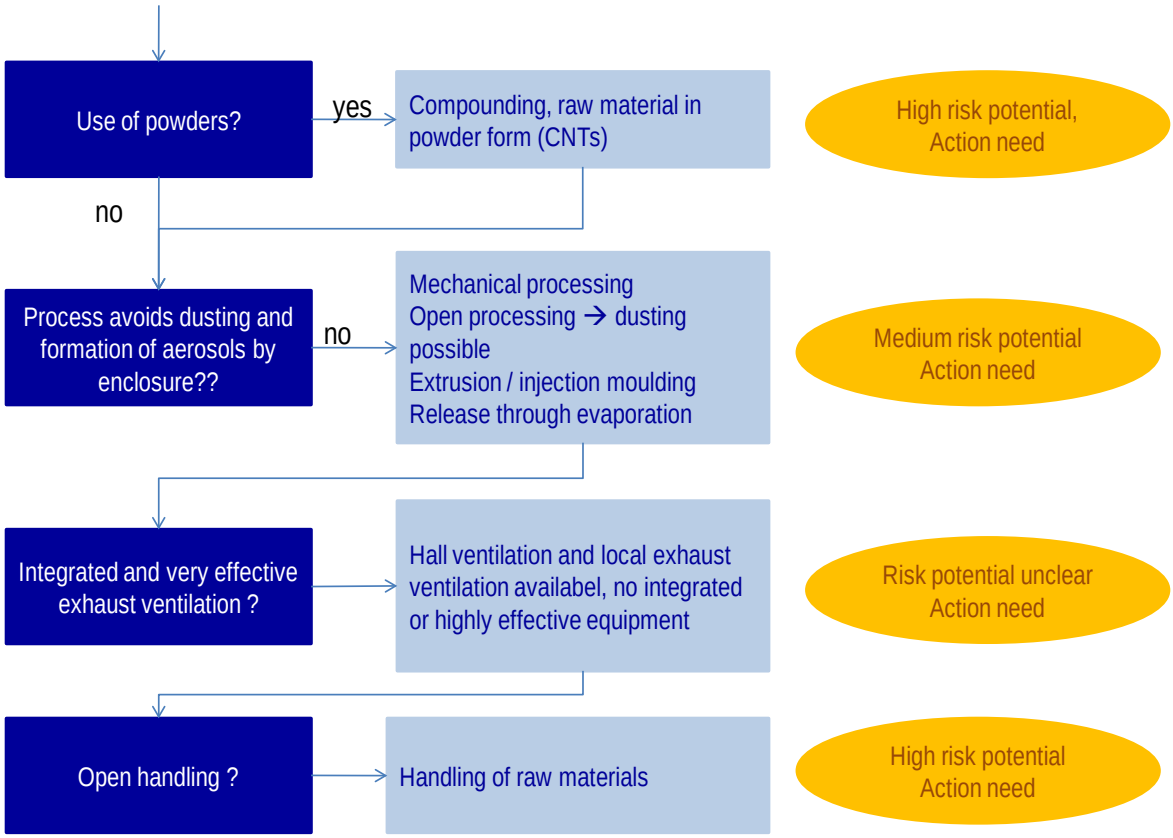

Figure 1: Assessment of risk potentials and derivation of action needs

3.3.6. Determination of protective measures

Based on the results of the qualitative risk assessment, ZBT identified the necessary protection measures, which should be implemented in a new production line, for the safe handling and use of CNTs. It became clear that an 'upgrade' of the 'old' production line was more difficult and costly than designing a new production line. Therefore, the following measures were planned and are implemented in the currently run 'new' installation.

Technical measures at source

- A glove box is installed for filling the CNTs into the extruder. Inside the glove box an air extraction system is integrated. The extracted air is led through a closed piping system to the overall exhaust system.

- The CNTs are entered into the glove box either in closed bags or barrels. After closure of the system, the bags or barrels are opened and entered into the gravimetry and afterwards released into the extruder. The emptied bags or barrels are closed and put into outer bags before they are taken out of the glove box and stored for final disposal.
- The extruder is a closed system with an integrated air exhaust system. Above the point of discharge of the polymer granulate from the extruder an additional local exhaust ventilation is installed.
- The injection moulding installation and the workbench for mechanical processing of bipolar plates are enclosed and an integrated exhaust ventilation system exists.

- All mechanical processing of the produced bipolar plates is carried out using local exhaust ventilation, because it is not fully clear whether or not particles could be released from the polymer material e.g. during sawing or drilling.

- The extracted air from all installations is collected into one exhaust gas system. The exhaust air is led through a washer (washing with water) inside a closed installation. The water solution potentially containing the nanoparticles remains inside the waste gas washer until disposal[7].

Organisational measures

- The workers are instructed to use protective clothing, respirators and goggles whenever working with CNTs to protect themselves in case of unforeseen incidents. Workers should not handle CNTs alone, and a second worker should always be present to ensure that quick action can be taken in case of such potential incidents.
- A separate workplace instruction exists for handling CNTs in compounding processes.
- The number of workers present in the rooms where CNTs are handled is limited during actual handling and processing by warning signs. Thereby, the number of potentially exposed persons is kept at a minimum.
- After processing of CNTs, the respective rooms are carefully cleaned according to the instructions of the manufacturer (vacuum cleaning with specific filter[8], wet sweeping). Also during cleaning, the use of protective clothes, respirators and gloves are required.

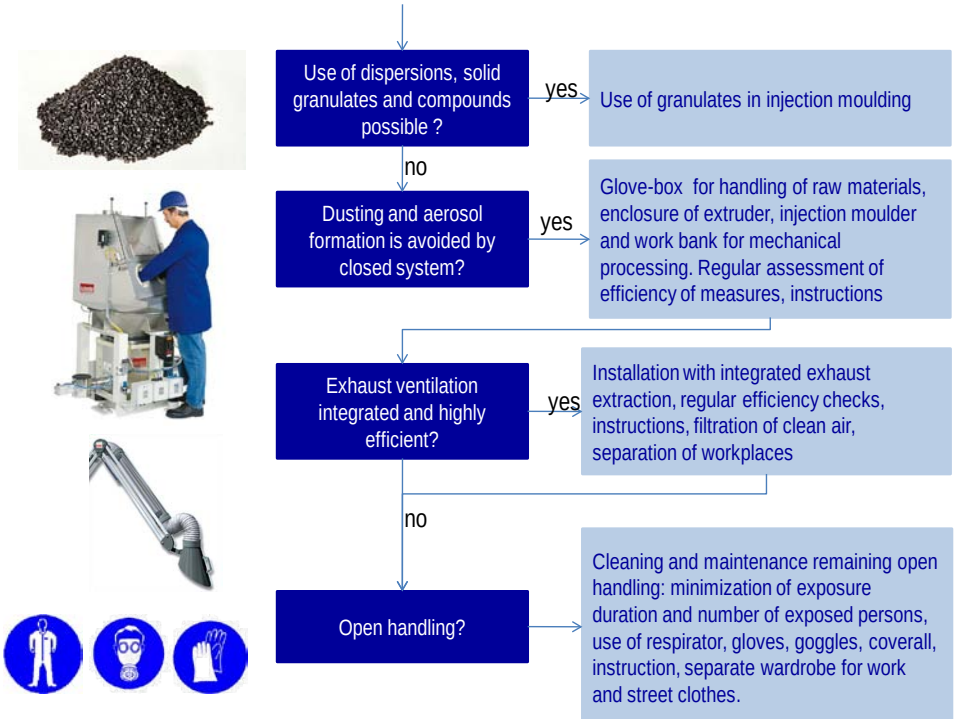

Figure 2: Scheme for the identification of protection measures

[7] Up to now, it was not necessary to dispose the filtration sludge.
[8] HEPA 14, dust class H)

3.3.7. Checking of efficiency of protection measures

The last step of the assessment process consisted in checking if the protection measures identified in the risk assessment are actually sufficient, to ensure that exposure levels are low and workers are not at risk.

The efficiency of the protection measures was controlled by air measurements. No measurements were regarded as necessary for the compounder / extruder, because the supplier conducted measurements under very similar conditions and with similar equipment. Therefore it was assumed that similar exposures would occur. Since the supplier could not detect CNTs in the workplace air at his extruder, the same was assumed for the extruder at ZBT.

The particle concentration in the workplace air at the injection moulding installation was identified using SMPS / CPC[9]. In addition, samples were analysed by scanning electron microscopy with regard to the particle morphology. In the air at the injection moulding installation, particle concentrations of < 35.000 / m^3 were detected. This number can hardly be differentiated from the particle background concentration. The microscopic analysis indicated that the detected particles are among others fractions of CNTs or respective aggregates.

Further measurements were conducted at the workbench and the milling equipment for mechanical processing of the finished plates by milling, drilling and sawing. In particular, during milling, relevant increases of particle emissions in the particle size range below 100 nm were identified. The emissions were visible. The analysis of the microscopy sample only in one case indicated that this could be fractions of CNTs. The majority of analysed particles however had no morphology like CNTs.

In total, from all measurements, it was deduced that the implemented protective measures sufficiently reduce and minimise the exposure of workers. It is regarded as unlikely that risks could occur to workers due to the use of CNTs in the given installation.

3.3.8. Information for workers

The workers at ZBT are regularly instructed in handling CNTs, how to operate the technical protective devices and use the personal protective equipment. The ZBT informed all employees about the results of the risk assessment. The concerns of all workers were thoroughly discussed and compared with the conducted analyses.

In addition, regular training is provided to all workers involved in the handling of CNTs, during the meetings for different research projects and conferences around the topic of CNTs and in the scope of current projects. The knowledge generated in these projects is disseminated to all employees in the topic area. Furthermore, general information events are organised at various times at ZBT.

3.4. What was achieved?

- The entire installation for processing CNTs was constructed to the highest and best technological standard regarding the protection of workers. The measures provide a high level of protection against all potential exposures. They are not specific for CNTs and therefore protect against exposure to other materials.
- The measures are implemented at the emission source. Organisational measures and personal protective equipment complement these measures, in particular with regard to unforeseeable incidents during the production process.
- The employees have gained a high level of trust in the efficiency of the protective measures because the risk assessment process and the checking of measures was done in a transparent way and well documented.
- The implementation of measures could be done very efficiently, because the risk assessment was integrated in the planning of the installation.

[9] Scanning mobility particle sizer / condensation particle counter

3.5. Success factors

- Close cooperation with the supplier of materials
- Implementation of the precautionary principle – despite the limited number of hazard indications, exposure was minimized and a high level of protection implemented
- Careful and continuous instructions of employees

3.6. Transferability

The process of a structured analysis of a material's hazards and the qualitative and quantitative exposure assessment and risk characterisation is applicable for all workplaces at which hazardous substances are handled.

The exposure measurements with SMPS/CPC and the analysis of the particle structure using REM is state of the art of the measurement technique and can be used at any workplace.

4. References, resources:

- Guide for activities with nanomaterials at the workplace (only German) (http://www.vci.de/template_downloads/tmp_VCIInternet/121717Leitf_Nano.pdf?DokNr=121717&p=101) or http://www.baua.de/de/Themen-von-A-Z/Gefahrstoffe/Nanotechnologie/pdf/Leitfaden-Nanomaterialien.pdf?__blob=publicationFile&v=3
- www.zbt-duisburg.de