Grouping of exposure and risk for processing of nanocomposites

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Abstract.
Several approaches had been performed to group similar properties of nanomaterials for the purpose of risk assessment. In addition to material and release properties, exposure during selected machining processes at workplaces was investigated. During exposure, transport and transformation processes between source and recipient also affect the materials. Ways of structuring the determination of risk are proposed for a risk assessment in activities involving nanomaterials in the workplace. The exposure during sanding of nanocomposites was found to depend on the matrix material rather than on the nano-additive.

1. Introduction

The German project nanoGRAVUR was performed to develop a framework for the grouping of nanomaterials concerning their risks in occupational, consumer and environmental context. Three tiers were addressed: tier 1 determines intrinsic physicochemical properties as well as the non-nanoform toxicity information (GHS classification) ("what they are"), tier 2 the extrinsic physicochemical properties like release from nano-enabled products and their toxic effects in in–vitro assays ("where they go"; "what they do"). If the first two steps leave an inconclusive assessment the third tier addresses case-specific testing to substantiate the similarity within groups or application-specific exposure testing [1].

In the course of this project the Institute for Occupational Safety and Health (IFA) performed the determination of exposure during grinding of selected nanocomposites. The goal was to investigate whether grouping of physical-chemical characteristics of nanomaterials can be chosen to categorise the exposure and thus the risk. Besides the exposure determination the assessment scheme for describing the risk at workplaces had been worked out. This includes information on material processing and concentrations at the workplace. Material properties like biopersistence, toxicity (for fibres determined by their flexural rigidity and modulating properties (agglomeration, critical dimensions, dustiness) have been grouped and class boundaries defined, leading to determine their hazard. Combining the information on hazard and exposure leads to the risk being allocated into three risk levels [2]. A scenario on application of nanofibres has been described [3]. The special needs for determining exposure to nano and micro sized fibres and selecting suitable groups according to their geometry and health impact are given in [4, 5, 6].

2. Methods

Composites on basis of epoxy resin, hardened cement mixtures, and aluminium with the additives of nano-objects from the groups of fibres (CNT, WS_2), platelets (graphene) and compact particles (TiO_2, SiO_2, carbon black) were chosen as materials for exposure testing. These composites were specifically produced for the project, either in plate form (epoxy resin 4mm thick and 80 mm broad, hardened cements 10 mm thick and 110 mm broad) or in slab form (aluminium 20 mm diameter, concrete 40x40 mm²). The investigated compounds and their content of nano-objects in the matrix material are stated in the Table, which are a subgroup of all materials investigated in the overall nanoGRAVUR project [1].

Sanding exposure tests were carried out with a belt grinder (7.25 m/s, belt size 100 x 914 mm², grade P240, P80 for one case only, aluminium oxide, Klingspor LS309X, Germany) in a ventilated test

chamber (4 m², 10 m³, 30 m³/h) for 15 to 20 min and three repeats each. The P 80 was used by two other groups in nanoGRAVUR.

Nanocomposite	Nano-objects added	Content of nano-objects in compound
Epoxy + SiO$_2$	SiO$_2$ (analogue to NM203_SiO$_2$_hydrophilic)	2.96 % by wt. (1.5 % by vol.)
Epoxy + CNT	CNT (NC7000, Nanocyl, multiwalled, different batch as NM400_CNT)	0.38 % by wt.
Epoxy + Graphene	multilayer graphene, thickness 2-10 nm, diameter 2-7 μm, ACS Material GNNP0052	1 % by wt.
Epoxy + WS$_2$	WS$_2$ inorganic nanotubes [7]	0.5 % by wt.
Epoxy + Carbon Black	carbon black Ensaco 250 G, Imerys	3.4 % by wt. (2 % by vol.)
Epoxy	-	-
Al + Graphene	multilayer graphene, thickness 2-10 nm, diameter 2-7 μm, ACS Material GNNP0052	3.39 % by wt. (~ 5 % by vol.)
Al + CNT	CNT (NC7000, Nanocyl, multiwalled, but different batch as NM400_CNT)	4.71 % by wt. (~ 5 % by vol.
Al	-	-
CEM_GGBS	GGBS (ground granulated blast furnace slag)	30 % by wt., water/cement ratio 0.4
CEM_HKP_GGBS_hr	HKP_GGBS_hr (highly reactive, nano-activated GGBS addition by high kinetic processing)	30 % by wt., water/cement ratio 0.4
CEM + SiO$_2$	NM203 SiO$_2$ hydrophilic or SiO$_2$ (analogue to NM203 SiO$_2$ hydrophilic)	1 % by wt., water/cement ratio 0.4 (with fluxing agent) and 0.55 (NM203 without fluxing agent)
CEM + TiO$_2$	NM102 TiO$_2$ nano active	1 % by wt., water/cement ratio 0.4 (with fluxing agent) and 0.5
CEM_hydr(ated)	-	-

Table: investigated nanocomposites for exposure testing, additional information in [1, 7, 8]; epoxy resin: DOW DER331; CEM_hydr: hydrated, dried and hardened clinker cement paste

The composite pieces were pressed with a force of approximately 15 to 20 N onto the sanding belt. Number and mass concentrations were determined inside the worker's breathing zone and in the near-field using several condensation particle counters (Grimm CPC 5.403, TSI CPC 3007), one aerodynamic particle sizer (TSI APS 3321), respirable dust samplers (FSP 2, FSP 10, GSA Messgerätebau, Ratingen, Germany, 2 and 10 l/min, 37 mm cellulose nitrate filter Sartorius 11301, 8 μm pore size), an inhalable dust sampler (GSP 10, GSA Messgerätebau, 10 l/min, 37 mm cellulose nitrate filter Sartorius 11301, 8 μm pore size), and a personal vertical elutriator for electron microscopy analysis (FAP, GSA

Messgerätebau, 2 l/min, 37 mm Nuclepore filters, 400 nm pores, gold coated) [2, 9]. Results of number and mass concentration were related to the area sanded on the compound piece due to the different geometries of the compound pieces.

Grouping the risk was performed on a parametrisation of the components hazard and exposure. Existing and new data on hazard of emitted material need to be used for the application of the risk evaluation scheme presented in chapter 4. The principle for addressing important factors and their grouping is described, but no examples or scenarios.

3.   Results and Discussion

Absolute particle number concentration in the worker's cabin ranged between 5600 and 23000 $1/cm^3$ (10 min average value) using P 240 sanding belt. This is in the low and medium exposure range of ultrafine particles measured in various industrial branches [10]. Normalising them to the processed surface of the composite block in order to take into account the different geometries of the compound samples the concentration span was from 8 to 130 $1/cm^3mm^2$ (Figure 1). Only the epoxy resin composites showed a decrease in normalised time-averaged particle number concentration by adding various nano-objects, with the lowest concentration observed at the WS_2 composite. The difference between lowest and highest concentration in this group of epoxy resins is about a factor of 4. The medium levels of the number concentration of the three composite groups are not far from each other, while the cement materials/composites exhibit the lowest level.

A comparison with release data on the same compound groups from two other partners in nanoGRAVUR [11, 12] revealed a different ranking for the cement compounds. There the number release rates in $1/mm^2$ s [11] and release concentrations in $1/cm^3$ [12], respectively, measured by CPC ranked from aluminium compounds (low) to epoxy resin compounds (medium) and cement compounds (high). Test conditions were different in using finer P 600 sanding paper [11], coarser P 80 [12] and a lower grinding velocity of 1.8 m/s for both research groups. Number concentrations of epoxy compound were about a factor of 5 higher than aluminium compound data [11] where this difference is not seen in Figure 1.

Cement compound data were a factor of 10 higher than epoxy resin data [11, 12]. Reasons for the different behaviour of the cement compounds are not evident. As the cement compounds show highest mass concentrations (Figure 2), a substantial part of the number of ultrafine particles could have been attached to the larger particles and thus lowering the number concentration during the sampling period of 20 min.
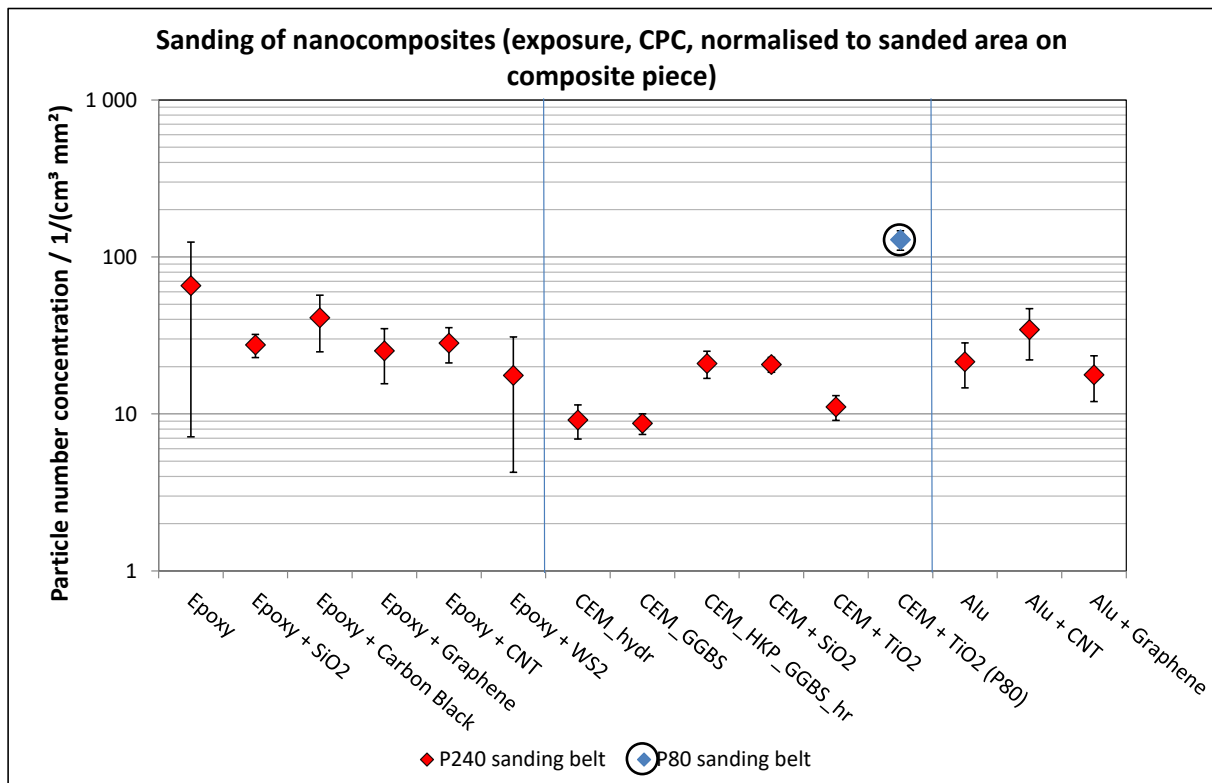
Figure 1: Number concentration during sanding of nanocomposites, normalised to the sanded area on the composite piece, size range appr. 4 nm to 3 μm, error bars show standard deviation of three replicates

Using a P 80 sanding belt reveals a substantial higher number concentration of a factor of 10, shown only in case of $CEM + TiO_2$. The reason is not evident. Temperature of the grinding belt was measured and did reach values of around 70 °C that will prevent pyrolysis effects of organic binder in the grinding belt. Large abrasive grains seem to have a different impact on the emission behaviour of ultrafine particles, which can also originate from the sanding belt, or the composition of P 80 is somewhat different from P 240.

The non-normalised respirable dust mass concentrations ranged from 0.6 to 46 mg/m³ in this specific setup, highest for cement composites, lowest for aluminium composites. Normalising the concentrations to the area that was ground on the composite pieces reveals the ranking given in Figure 2. A piece of pure concrete (without nanomaterial) was also subject to grinding as a comparison to the hardened cement paste composites. Pure concrete showed a much smaller release/exposure. Inhalable dust compared to respirable dust was about a factor of 4 higher. The respirable dust was sampled with a cyclone (FSP 10) having a cut-off at 4 μm aerodynamic diameter (50 % value).
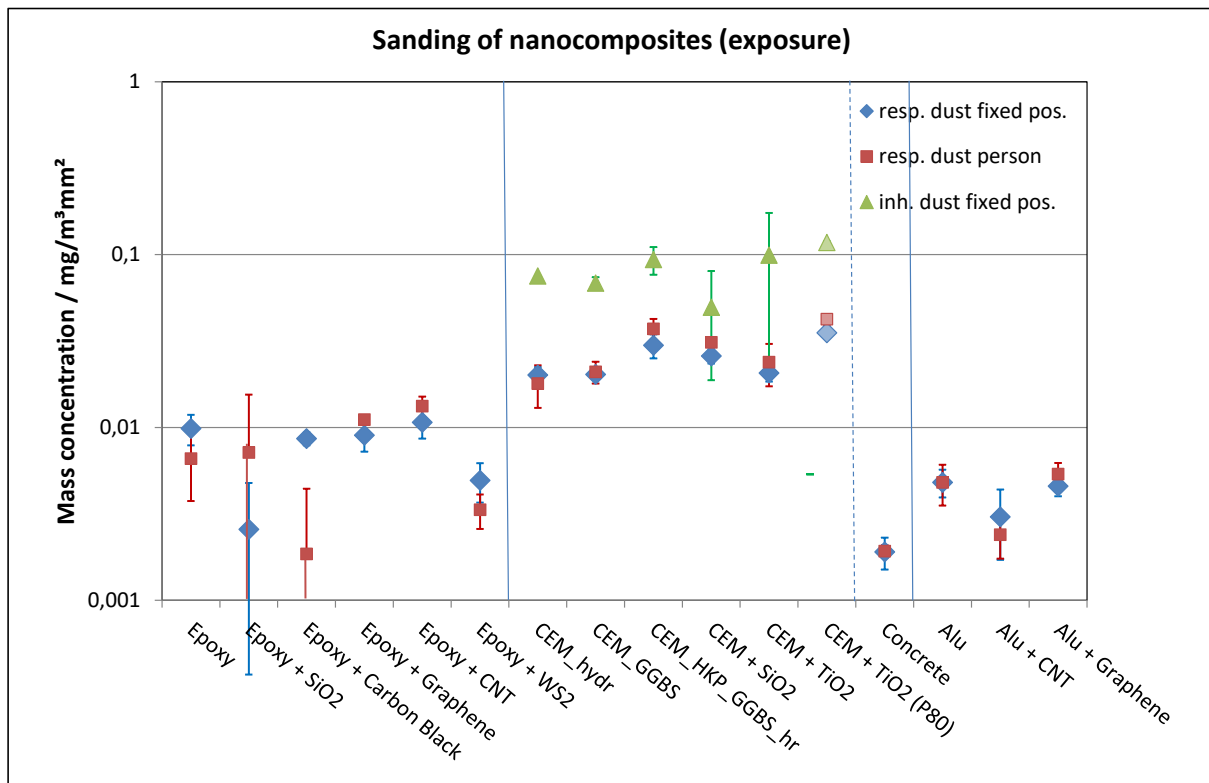
Figure 2: Mass concentrations during sanding of nano-composites, respirable and inhalable dust measured at the person and in its near-field (fixed position), normalised to the sanded area of the composite piece, error bars show standard deviation of three replicates

The influence of the internal matrix material structure with its respective properties values for mechanical resistance dominates the ranking. The hardened cement pastes (without sand and coarse grain filler used in concrete) has the weakest internal structure that lead to the higher exposure concentrations. Aluminium is seen on the opposite side, leading to low exposure concentrations. The added nanomaterial was a lesser influencing factor for the exposure than the matrix material, which is in accordance to pure release measurements in the nanoGRAVUR project [11].

An aerosol sample (sampler FAP) from grinding epoxy resin plus CNT is taken as an example for a nanofibre additive and analysed by SEM and EDS. An overview of the particles in the breathing zone of the worker is shown in Figure 3. Part 3 a displays the general morphology, 3 b the element mapping of carbon (yellow) and aluminium (red). The particles are carbon-based and thus belong to the matrix material of the nanocomposites, in this case epoxy resin. Small aluminium spots (red) cover uniformly the whole surface of the sample while being unclear whether this material appears as independent nanoparticle on the sample or covering the surface as condensed material.
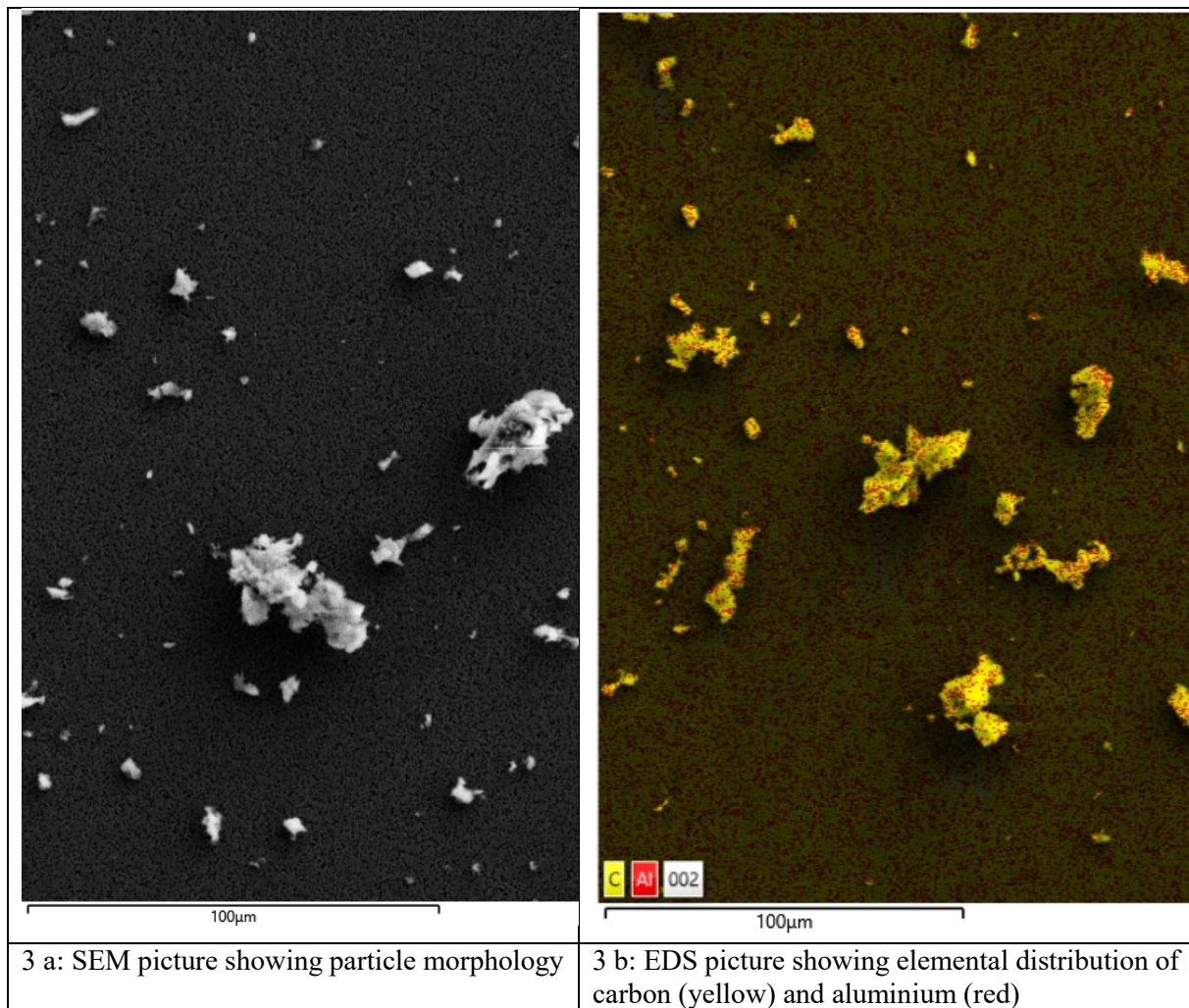
3 a: SEM picture showing particle morphology	3 b: EDS picture showing elemental distribution of carbon (yellow) and aluminium (red)

Figure 3: SEM and EDS analysis of aerosol particles in the breathing zone of the worker, sanding of epoxy resin plus CNT

Occurrence of metal elements on the sanding belt surface was analysed as aluminium, sodium, iron (sequence of main occurrence high to low). This finding supports the fact that cryolite (Na_3AlF_6) was used as binder in the sanding belt (1 to 9 % in that product series according to manufacturer), while aluminium and probably sodium being transferred onto the filter surface. It is not clear how much such an effect of nucleation could contribute to the total number concentration measured with the CPC. Measurements with a Scanning Mobility Particle Sizer (SMPS) indicate the highest number concentrations at the lower edge of the particle size measurement interval at 18 nm, supporting such a nucleation mode [2].

No isolated nanofibres or their agglomerates were observed. In contrast, composite particles with protruding single CNT were regularly observed (Figure 4). The fibrous objects show parallel edges and their diameter of 15nm on average corresponds to that of the CNTs used in the nanocomposite material. Their protruding length (here appr. 200 nm) is usually shorter than the original CNT length because of the shear forces during grinding applied by the abrasive grains. Only a single study reported occurrence of isolated nanofibres due to grinding [13].
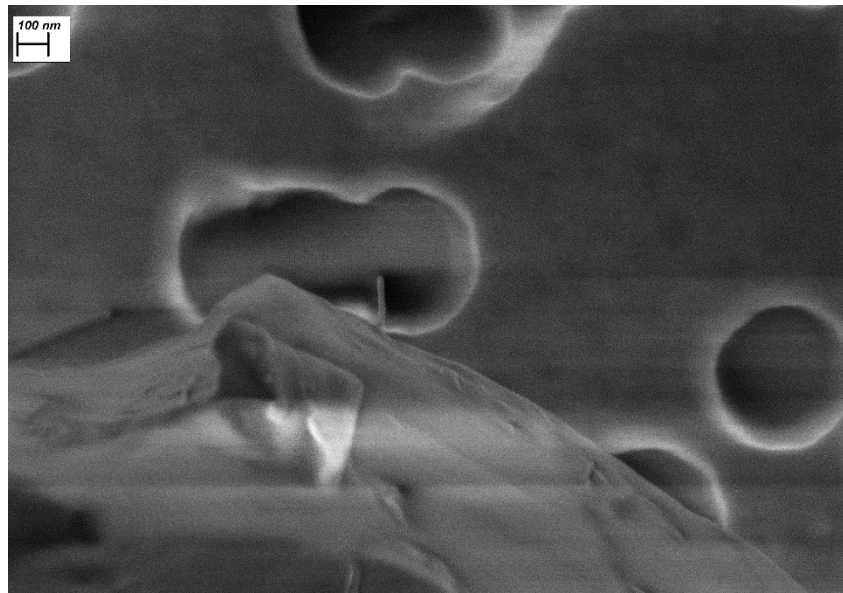
Figure 4: Abraded particle from sanding epoxy resin plus CNT, protruding nanofibre

4. Risk grouping

A workplace risk assessment scheme based on the concept of "hazard x chance of exposure = risk" was developed. Properties describing hazard and exposure are banded and each band represented by scoring [6] (Figure 5).
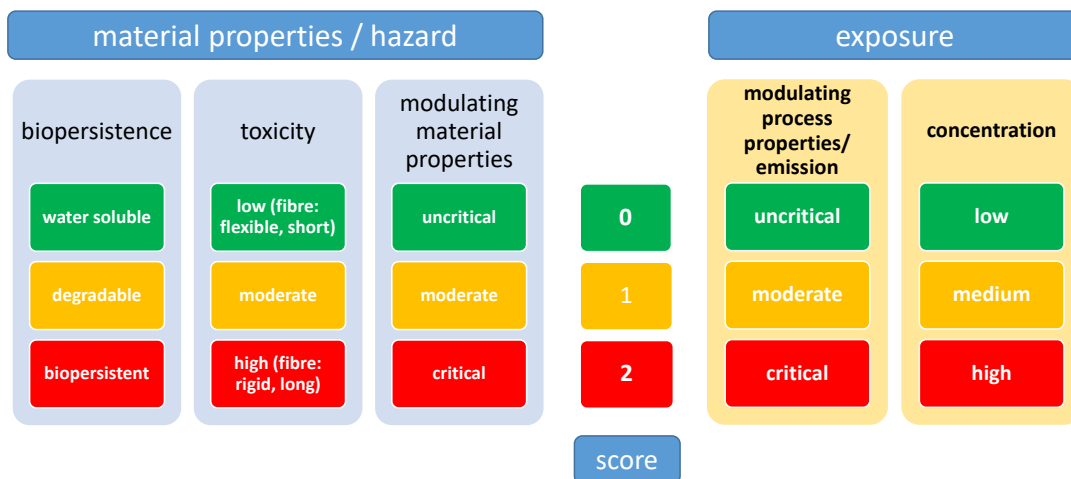

Figure 5: Banding approach for hazard and exposure properties

The total scores for hazard and exposure yield the placement in a score-matrix, i.e. risk matrix. To keep the application of the risk matrix practicable, the hazard score is entirely based on literature values from material testing, e.g. water solubility (OECD Draft Guidance Document on Determination of solubility and dissolution rate of nanomaterials in water and relevant synthetic biological media, OECD Joint WNT/WPMN Expert Group on physical-chemical properties of nanomaterials, Project 1.5, to be published 2022) and degradation in physiological media [14]. These data allow predicting the biopersistence [15] of the material as well as its toxicity, which depends hypothetically on length and rigidity in case of biopersistent fibres [16]. Modulating factors of the hazard can be aggregation/agglomeration effects leading to larger objects with probably lower hazard potential, the existence of critical dimensions, especially fibre forms, or dustiness properties of the material in use

(Figure 6). Critical dimensions for fibres are the so-called WHO-criteria (length > 5μm, diameter < 3 μm and aspect ratio >3). Dustiness can be tested following testing protocols given in EN 17199 for powdery nanomaterials [17] and the fluidizer dustiness test for fibres [18]. Mass and number based values for dustiness in dependence of the input energy of the process were tested in nanoGRAVUR [1, 11] and group boundaries proposed.

Figure 6: Modulation properties for determining the hazard of nanomaterials, with scoring

Exposure is described by the determination of the quality of the release with its modulating properties and the quantity of release at the position of the receptor (= worker) taking into account the transfer from the process to the worker. Modulating properties describe the capability of the process (e.g. grinding a composite) to produce critical dimensions of nano-objects and its release characteristics including aggregation/agglomeration effects. Emission values should be measured or can be indicated by expert judgement. Several control banding tools use to describe processes in terms of their potential to release dust. These categories, e. g. "high energetic process = high emission" can be used to estimate the emission. An example for these categories is proposed for different source domains and their respective multipliers which reflect the propensity of a process to release nano-objects [19]. Such data are used in control banding tools. If only powders are processed the assessment of the dustiness and agglomeration effects is to be applied here instead for the material properties.

The second factor for exposure is the measured concentration at the worker which can be assessed with occupational exposure limit values. Note that the workplace concentration is a generalized term that requires clear definition in the context of the exposure assessment. For example, general dust is measured as a shift-averaged mass concentration whereas the exposure to fibres is assessed by determining the shift-averaged number concentration of particles matching the WHO-criteria.

The result of the juxtaposition of both scores gives a matrix with risk levels following the scheme of a traffic light (Figure 7). Green predicts low risk and the protective measures are sufficient for safe work. Yellow for moderate risk is an indicator that current safety measured need to be examined for effectiveness. Red for high risk instructs the safety manager to increase protective measures, e.g. following the German TRGS 527 [20]. Further experience with this control banding approach by grouping the properties has to be discussed in future.
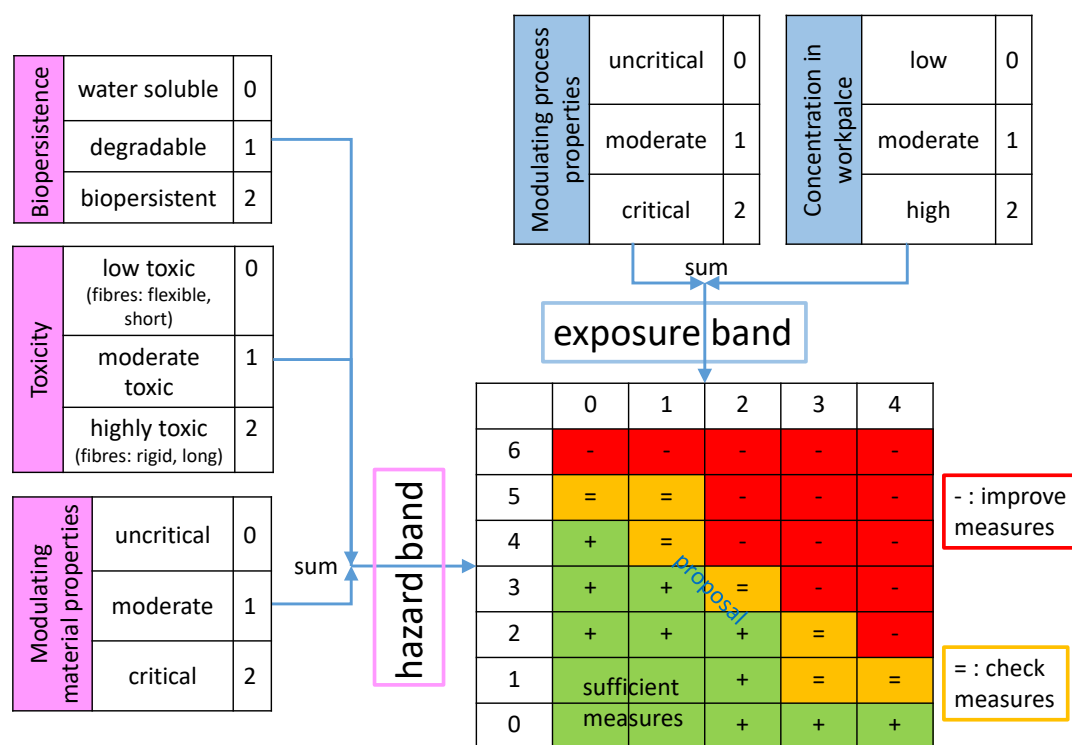
Figure 7: Risk assessment scheme for nanomaterials

5 Conclusions

Categorizing the exposure as well as the release to processing nanocomposites revealed the main dependence on the matrix material and its mechanical properties and less dependence on the nano-additive. Average absolute number concentrations of the submicrometer particles ranged between 5600 and 23000 $1/cm^3$. Only the compound group of epoxy resins showed a decrease up to a factor of 4 in number concentration with adding different nanomaterials. The mass concentrations for the respirable dust fraction (at the person and near-field) was different with the type of matrix material and highest at the group of cement composites. A significant dependence of the mass concentration on the nano-additive was not detected.

For the assessment of the risk associated with activities involving nanomaterials at the workplace, the suggestions for structuring the identification of risk presented in the article can be used. They are divided into the evaluation of material, hazard, release and thus exposure properties. Overall, the results from nanoGRAVUR can help to expand the use of groupings in areas such as occupational safety, product labelling and regulation, where assessments are done on basis of single case studies at present. The application of the risk assessment will give feedback to the grouping characteristics. Further exposure scenarios are needed to gain experience with these tools.

Acknowledgements

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