IFA
Institut für Arbeitsschutz der
Deutschen Gesetzlichen Unfallversicherung

**Translation of:**

*Hellmann, A.; Schmidt, K.; Ripperger, S.; Berges, M.:* Freisetzung ultrafeiner Stäube bei der mechanischen Bearbeitung von Nanokompositen. Gefahrstoffe – Reinhalt. Luft 72 (2012) No. 11/12, p. 473-476. (by courtesy of Springer-VDI-Verlag, Düsseldorf)

## Release of ultrafine dusts during the machining of nanocomposites

A. Hellmann, K. Schmidt, S. Ripperger, M. Berges

### Abstract

The present study investigates the release of ultrafine particles during the grinding of nanocomposites. Used as the test material was epoxy resin (ER) with carbon nanotubes (CNTs), which was machined by hand on a commercially available double grinder. The particle number concentration and size distribution of the released dust were measured, with special consideration given to CNTs. A scanning mobility particle sizer and a condensation particle sizer were used for measurements. Particle separation was performed with a Nanometer Aerosol Sampler and an Electrical Low Pressure Impactor. The results showed that the largest fraction of the measured particle number concentration during and after grinding was in the submicron range. Released particles of the employed compound material with CNTs revealed isolated CNT-ends on the surfaces of the particles. This phenomenon was not observed with pure epoxy resin. The possible release of individual free CNT fibres was not detected.

## Freisetzung ultrafeiner Stäube bei der mechanischen Bearbeitung von Nanokompositen

### Zusammenfassung

In der vorliegenden Arbeit wird das Schleifen von Nanokompositen hinsichtlich der Freisetzung von ultrafeinen Partikeln untersucht. Als Testmaterial dient Epoxidharz mit Carbon Nanotubes (CNT), das von Hand mit einer handelsüblichen Doppel-Schleifmaschine bearbeitet wird. Im freigesetzten Staub wird die Partikelanzahlkonzentration und -größenverteilung vermessen,

unter besonderer Berücksichtigung der CNT. Für die Messungen wurden ein Scanning Mobility Particle Sizer und ein Condensation Particle Sizer verwendet. Die Partikelabscheidung erfolgte über einen Nanometer Aerosol Sampler und einen Electrical Low Pressure Impactor. Hierbei zeigte sich, dass der größte Anteil der gemessenen Partikelanzahlkonzentration während des und nach dem Schleifen im submikronen Bereich lag. Freigesetzte Partikel aus dem verwendeten Material mit CNT wiesen vereinzelte CNT-Enden an der Oberfläche der Partikel auf. Bei reinem Epoxidharz konnte dies nicht beobachtet werden. Eine mögliche Freisetzung einzelner freier CNT-Fasern wurde nicht festgestellt.

## 1 Introduction

Nano-objects ranging in size from 10 to 100 nm in at least one dimension are being increasingly added to polymer materials during processing as reinforced materials. Their addition gives rise to so-called nanocomposites that have strength parameters superior to those of pure polymer materials. The reinforced materials employed, with primary particle sizes ranging from 10 to 100 nm, include titanium oxide ($TiO_2$), aluminium oxide ($Al_2O_3$), zirconium oxide ($ZrO_2$) and silicon oxide ($SiO_2$). Polymer materials are also reinforced considerably through the integration of carbon nanotubes (CNTs). On the rotors of wind turbines, the increase in strength reduces the necessary cross-sectional areas, which yields weight savings that diminish the rotors' inherent load. The addition of CNTs also increases electrical conductivity. So that such improvements are actually manifested,

- the agglomerates or clusters that are formed in the reinforced materials have to be broken up as far as possible into the various nano-objects,
- the individual objects have to be distributed as uniformly as possible in the polymer material and
- the objects have to be fully enclosed by the polymer material.

Since nano-objects tend to exist as agglomerates or aggregates, development work is still in progress to satisfy the requirements listed above as far as possible. To disperse the objects in highly viscous liquids or melts, the dispersing systems familiar in particle process engineering, e.g. dissolvers, colloid mills, agitator ball mills [1] and ultrasonic dispersers [2], are being investigated and put to use.

In connection with occupational health & safety and environmental issues, it is important to find answers to the following questions:

- Can individual nano-objects be released from nanocomposites?
- If they cannot, which size and structure do the released particle clusters have?
- If they can, how quickly do the nano-objects agglomerate into particle clusters?
- Is it possible to develop useful test procedures to determine the release potential?

Processes that could conceivably cause the release of nano-objects are:

- Ageing or weathering processes that can cause decomposition reactions on the near-surface plastics matrix, thus exposing the finely distributed nano-objects. On exposure to strong solar radiation, plastics surfaces, for instance, can then become brittle and fissured. Acids (e.g. acid rain) and other chemicals can intensify such unfavourable changes.
- Micromechanical stressing processes during product use, as occur, for example, during sliding and rolling friction in the stressed near-surface zones.
- Machining processes such as sawing, milling, drilling and grinding.

The long-term behaviour of nanocomposites is also of interest in connection with the use and disposal of products manufactured from them.

The characterisation of particles released during the machining of nanocomposites has already been the subject of several scientific studies. *Vorbau* et al. [3] used the Taber Abraser test device for their tests. *Göhler* et al. [4] set up a test rig with a rotating cylindrical grinding element that was guided from below along the coated surface being tested. *Wohlleben* et al. [5] experimented with a Taber Abraser, a grinding wheel and a UV lamp. They also investigated a number of different nanocomposites. *Stahlmecke* et al. [6] investigated particle release during the machining of materials with hand-held electric power tools. *Golanski* et al. [7] also studied particle release from nanocomposites with different machining methods.

In all of these studies, the particle size distribution of the generated aerosol was ascertained with an aerodynamic particle sizer (APS), scanning mobility particle sizer (SMPS) or fast mobility particle sizer (FMPS). The total number concentration was determined with a condensation particle counter (CPC). *Kuhlbusch* et al. [8] present a comprehensive overview of the scientific studies that have so far been published on the subject and particularly on the measuring methods employed and substance systems investigated.

It has been discovered that, in the case of nanocomposites, the nanoparticles are mainly released in an agglomerated state with the matrix material. It has also been found that the particles released from a nanocomposite and from a material without reinforcing particles differ in shape, size and number.

## 2 Our own studies

In order to investigate more closely the possible particle size distribution, particle concentration and particularly the possible shapes and structures of released particles of nanocomposites containing CNTs, an experimental set-up with a commercially available double grinder was established and manual grinding tests were carried out. Grinding with grinding wheels is a removal process with cutting edges that are formed by the respective shapes of the hard grains of the grinding wheel. Depending on the pressing force and grinding wheel structure, topography and rotary speed, a greater or lesser mass of material is removed and finely dispersed in the air. Depending on the design of the grinder, extractor and type of work process, the machine operator may be directly exposed to the generated aerosol. For an assessment of occupational health, details of the number concentration, size distribution and shape of the airborne particles are therefore necessary.

## 3 Experimental set-up

Particle generation by grinding takes place in a sealed glove box in which the double grinder is mounted. Within the box, different material specimens can be manually machined. For removal of the released particles, an air flow passes through the box. To this end, compressed air which has already passed through an adsorber and a fine filter is taken from the compressed air network and fed for final cleaning through a High-Efficiency Particulate Air (HEPA) filter. The downstream equipment is supplied with the now virtually particle-free air flow.

With the part stream that flows through the glove box, part of the particle-laden air is sampled. The various measuring instruments are supplied with the sampled air. These are usually a condensation particle counter (CPC, models 3022 and 3775 from TSI), a scanning mobility particle sizer (SMPS, model 3934 from TSI), a nanometer aerosol sampler (NAS, model 3089 from TSI) and an electrometer (model 3068B from TSI). The required air flow of 3 or 32 $l \cdot min^{-1}$ (collected by the NAS or ELPI from Dekati) is set with a flow meter (model 4043 from TSI). The excess aerosol is discharged via an end filter. **Figure 1** shows a simplified schematic diagram of the experimental set-up.

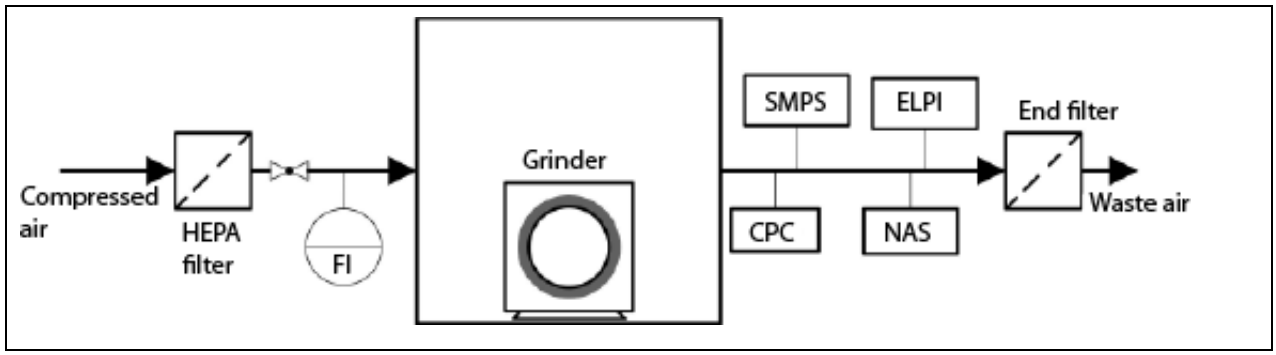


Figure 1:
Schematic of experimental set-up. *FI: flow meter*

## 4 Materials used

For the tests presented here, specimens of epoxy resin were ground. Some of the specimens were reinforced with 0.5 vol. % multi-walled carbon nanotubes (MWCNTs, Baytubes® C 150 P). A single CNT fibre has an outer diameter ranging from 5 to 20 nm and can be over 10 µm long. In an elaborate multi-stage process, the CNTs were distributed in the epoxy resin as finely as possible. The specimen material containing CNTs gains a black colouration as a result. If, on the other hand, a metal or metal alloy is reinforced with CNTs, no definite visual changes are manifested at all.

## 5 Test performance and results

Before the proper tests, the box was tested for tightness. Furthermore, the scale of particle release from the grinder in a dummy run was also investigated. To this end, treated air was first fed through the box and the grinder was switched on. In a preliminary test, the particle number concentration within the box and in the discharged air was measured with a CPC in each case. **Figure 2** shows the measured particle number concentration over time (without applying a material).

First of all, the grinder is switched off. It can be seen that existing particles are ejected with the treated air due to the air flow through the glove box and the particle number concentration falls to almost zero. When the grinder is switched on, the concentration rises abruptly to 12 particles/cm$^3$ and then drops again due to the air flow. There are no significant differences with changes in the sampling position. When a very low particle concentration has again been reached, the proper grinding test starts. To this end, a specimen is briefly and repeatedly pressed by hand against the rotating grinding wheel. The measured changes in particle concentration are shown in **Figure 3**.

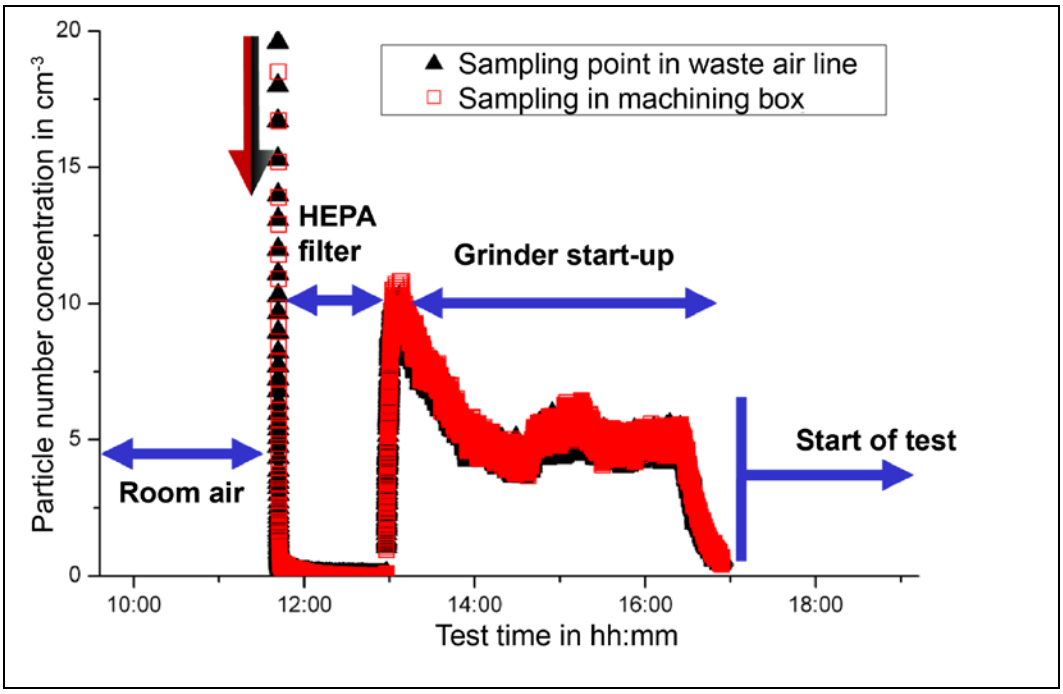


Figure 2:
Particle concentration over time during preliminary test

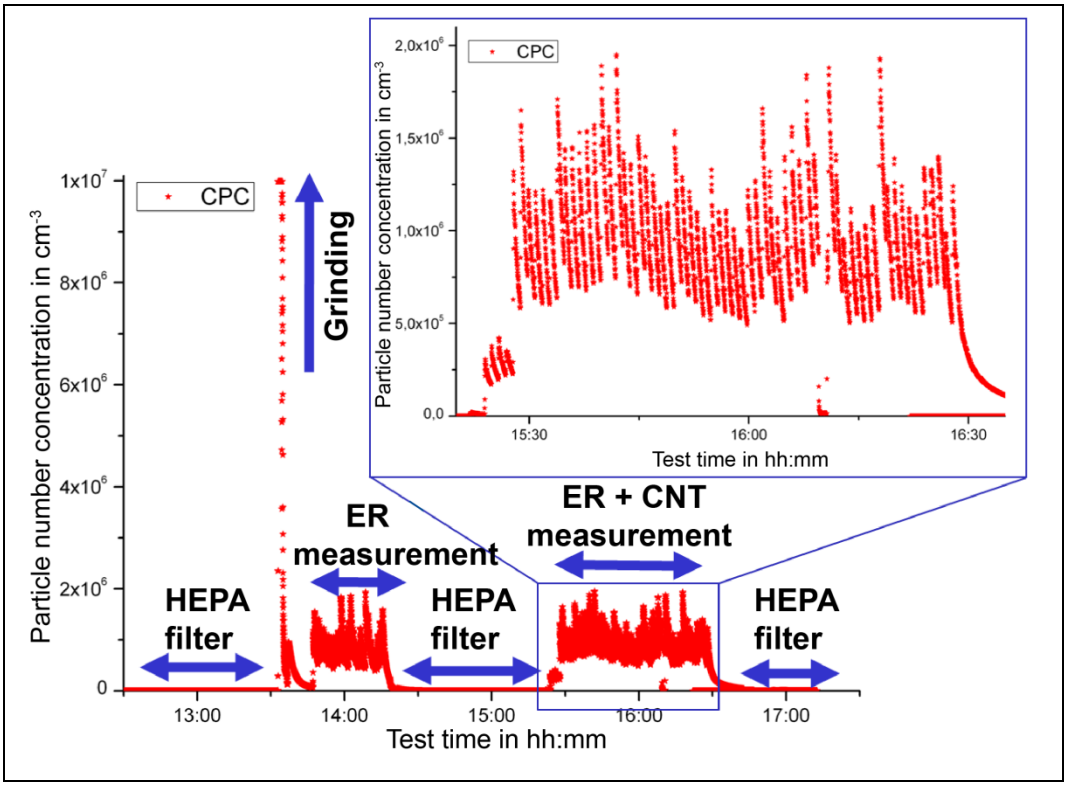


Figure 3:
Overall particle number concentration measured during the grinding of pure and CNT-reinforced material

In the periods marked “HEPA filter”, grinding was not performed. It can be seen that a high particle concentration is achieved during only very brief grinding. During grinding, care was taken that the material does not change significantly due to the effects of temperature and that the particle concentration is still within the CPC’s measuring range which ends at $10^7$ particles/cm$^3$. A sample of pure epoxy resin was ground in the period marked “ER” in Figure 3, and an epoxy resin sample reinforced with CNTs in the period marked “ER + CNT”.

During grinding of the material, the particle count increases depending on the nature of the above-mentioned parameters of the grinding process. **Figure 4** shows the measured particle size distributions (SMPS) after the end of the grinding process. The particle number concentration is plotted over time. The smaller graph shows the particle number concentration logarithmically over particle size for three points in time. Particles were detected across the entire measurement range of the SMPS. The mode for particle diameter is about 30 nm. The decline in particle concentration is due to the dilution air flow, sedimentation and coagulation within the glove box.

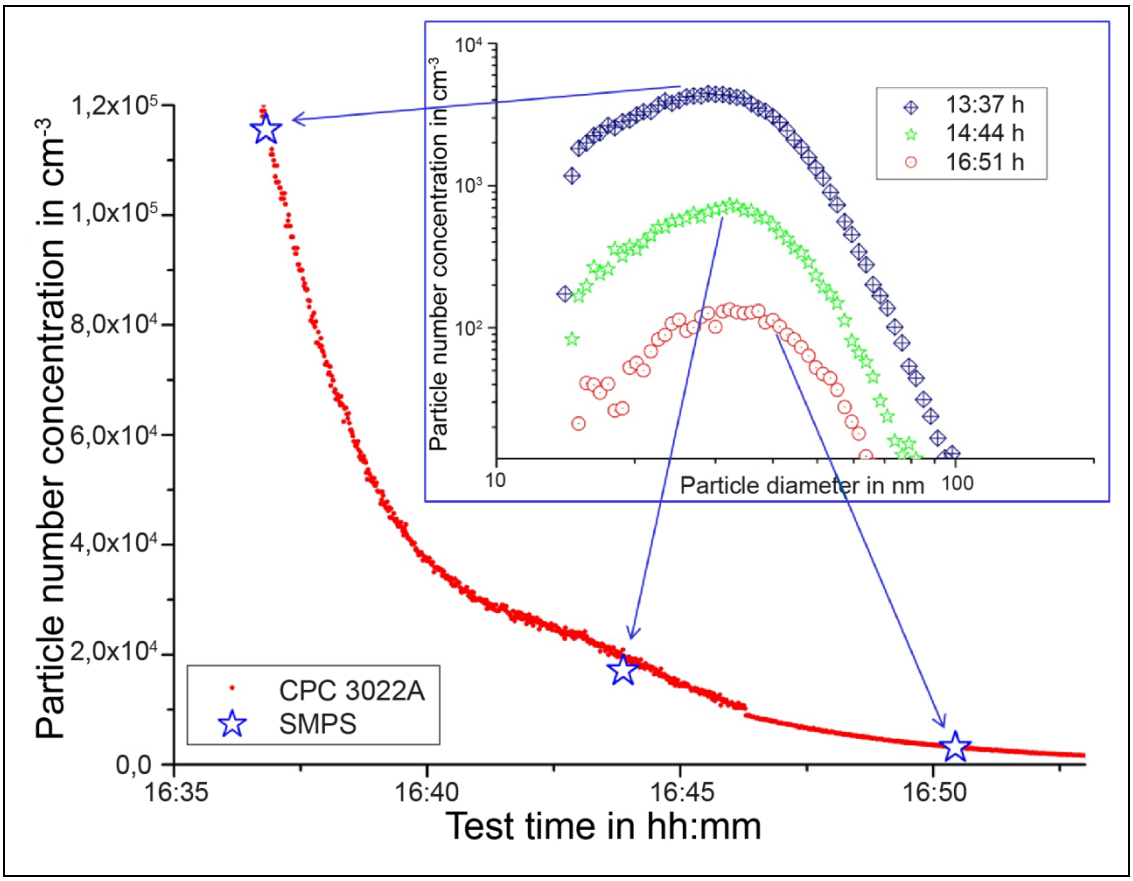


Figure 4:
Particle size distribution measured with the SMPS during the flushing process after grinding

During the grinding process, generated particles were sampled with an NAS (sampling time up to 5 min, air flow rate 1.5 l · $min^{-1}$, electrode voltage approx. 9.4 kV). The separated particles were then studied under a scanning electron microscope (SEM). **Figure 5** shows the SEM images.

From the images, it can be seen that, during sampling, particles > 1 µm were also separated in the course of grinding. Quantitatively, however, they are negligible compared to the many sub-micrometre particles. For particles of composites containing CNTs, exposed fibre ends protruding from the particles are visible. Without added CNTs, no particles were found with exposed or fibre-like structures.

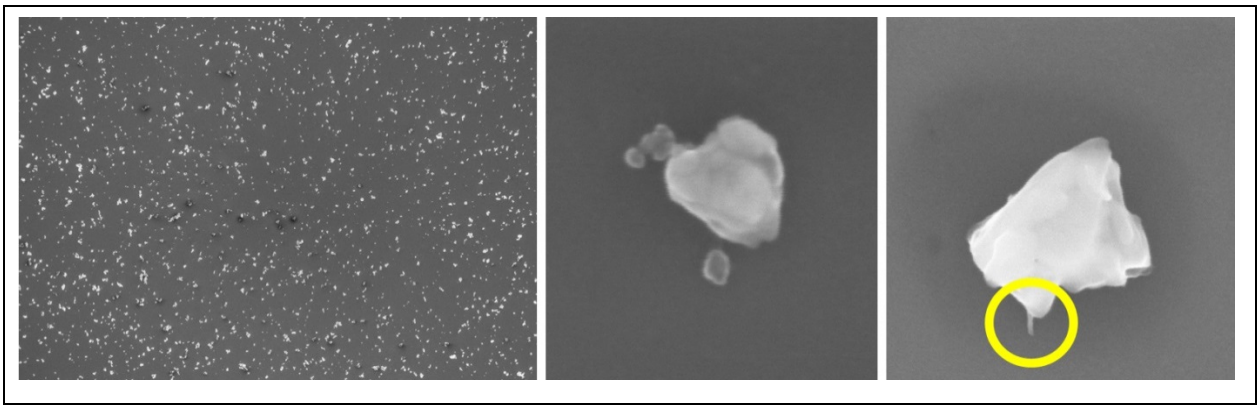

Figure 5:
SEM images of an epoxy resin particle distribution (left) and
single particles without (centre) and with CNTs (right)

Particle separation was performed not only with the NAS, but also with a cascade impactor, electrical low-pressure impactor (ELPI) from Dekati. As a result, a higher sampling flow rate of 30 l · $min^{-1}$ out of the glove box was achieved, the air flow being guided straight through the impactor. This meant that all the stages of the impactor were sufficiently charged with particles of the associated sizes. The particles were separated on aluminium foil and studied with a SEM. **Figure 6** shows an image sequence of separated particles with 5,000x, 25,000x and 90,000x magnification, generated during the grinding of an epoxy resin sample reinforced with CNTs. Upwards of a magnification >50,000x, single CNTs can be seen on epoxy resin particles. Single detached or exposed CNTs were not found. The toxicological assessment of these particle shapes still has to be performed.

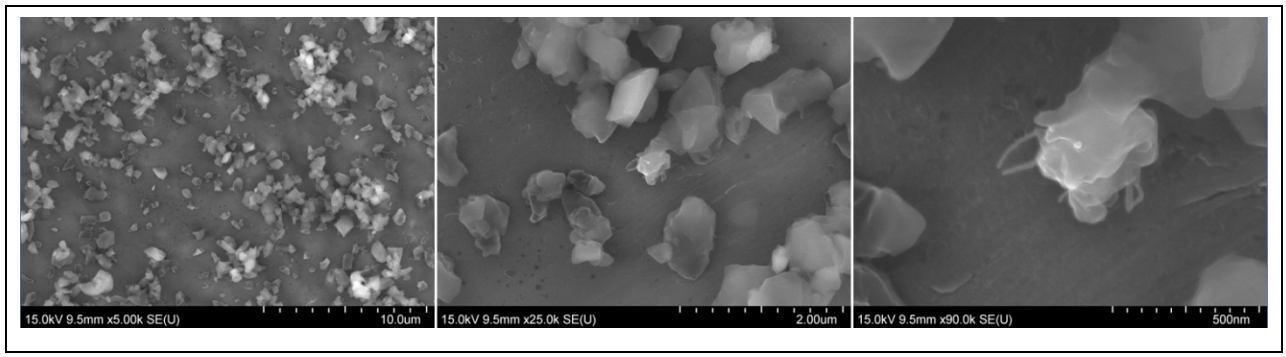


Figure 6:
SEM images of epoxy resin particles containing CNTs on aluminium foil with different degrees of magnification

**References**

[1] *Englert, M.:* Einfluss mechanischer Dispergierverfahren auf Struktur und Eigenschaft duroplastischer Nanoverbundwerkstoffe. Dissertation Technische Universität Kaiserslautern, 2009.

[2] *Bittmann, B.-A.:* Ultraschalldispergierung von anorganischen Nanopartikeln in Epoxidharz und Charakterisierung der resultierenden Werkstoffeigenschaften. Dissertation Technische Universität Kaiserslautern, 2008.

[3] *Vorbau, M.; Hillemann, L.; Stintz, M.:* Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings. Aerosol Sci. 40 (2009), p. 209-217.

[4] *Göhler, D.; Stintz, M.; Hillemann, L.; Vorbau, M.:* Characterization of nanoparticle release from surface coatings by the simulation of a sanding process. Ann. Occup. Hyg. 54 (2010) No. 6, p. 615-624.

[5] *Wohlleben, W.; Brill, S.; Meier, M. W.; Mertler, M.; Cox, G.; Hirth, S.; von Vacano, B.; Strauss, V.; Treumann, S.; Wiench, K.; Ma-Hock, L.; Landsiedel, R.:* On the lifecycle of nanocomposites: comparing released fragments and their in-vivo hazards from three release mechanisms and four nanocomposites. Small (2011) No. 7, p. 2384-2395.

[6] *Stahlmecke, B.; Romazanov, J.; Asbach, C.; Fissan, H.; Kuhlbusch, T.:* Investigations on (Nano-)particle release during mechanical treatment of different composite materials. European Aerosol Conference, Manchester, 2011. www.eac2011.com/scientific-programme

[7] *Golanski, L.; Guiot, A.; Pras, M.; Tardif, F.:* Release-ability of nano fillers from different nanomaterials. European Aerosol Conference, Manchester, 2011. www.eac2011.com/scientific-programme

[8] *Kuhlbusch, T.; Asbach, A.; Fissan, H.; Göhler, D; Stintz, M.:* Nanoparticle exposure at nanotechnology workplaces: A review. Part. Fibre Toxicol. (2011) No. 8, p. 22.

M. Sc. Albert Hellmann, Dr.-Ing. Kilian Schmidt, Prof. Dr.-Ing. Siegfried Ripperger,
Lehrstuhl für Mechanische Verfahrenstechnik, Technische Universität Kaiserslautern.

Dr. rer. nat. Markus Berges,
Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA), Sankt Augustin.