

Nanoparticle release quantification of sanding-induced airborne particle emissions from artificially aged/weathered nanocomposites

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ABSTRACT

Defined sanding-processes were simulated for the characterization of the (nano)-particle release into the air from surface coatings (SC) and solid materials (SM) containing different nanoscaled pigments (NSP) and nanoparticle additives (NPA). Systematic analyses were performed for artificially aged/weathered samples.

Results have shown that the sample material, the sample composition, the sample condition and especially the treatment procedure have a strong impact on the particle release. Despite occasional high numbers of released nanoparticles, no free isolated NPA or NSP could be observed during extensively performed SEM-, TEM- and EDX-analyses.

Keywords: nanoparticle release, nanocomposites, artificial aging / weathering, exposure, EHS

1 INTRODUCTION

Possible risks of substances to health, safety and environment depend on the coexistence of material toxicity and material exposure [1]. The increasing production, processing and use of nanomaterials require an extended risk assessment taking into account the material's dispersing state. In this context, systematic exposure studies on nanocomposite materials (NCM) in laboratory can provide basic data about the ability and the quantity of nanoparticle release into the air [2].

NCM, where synthetic nano-objects are embedded in a solid surrounding matrix, has become increasingly important for plastics materials and coatings. Numerous laboratory exposure studies attempted to demonstrate whether embedded nano-objects can be released into the air from the matrix material by mechanical treatment. Most have shown, that engineered nano-objects are firmly embedded in released wear or swarf [2]. Exceptions [e.g. 3] may be based on non-optimal sample preparation and/or conditioning like incomplete wetting, incomplete or no surface modification. A release of sufficiently high amounts of isolated nano-objects from well-prepared NCM seems only be possible by prior chemical or thermal degradation of the matrix material [4].

Natural matrix material degradation with potential exposing of embedded nano-objects can arise from weather-caused impacts. Until now, only a few studies [e.g. 4-7] have dealt with nano-object exposure characterization during or after artificial matrix material degradation. In this context, two projects (A, B) were performed to get a deeper insight in the sanding-induced particle release behavior of NCM during their life-cycle.

2 MATERIALS AND METHODS

2.1 Sample preparation and conditioning

Project A. The coatings of project A were exactly the same as analyzed and described in prior work [9, 10], i.e. three different matrix materials (two-pack polyurethane coating: PU^A, white-pigmented acrylate coating: AC^A; UV-curable clearcoat: UV^A) in combination with a NPA (zinc oxide: ZO) and respectively with a NSP (iron oxide: EO). The coatings were applied on substrates (fiber cement plates for AC^A, oak plates for PU^A and UV^A, aluminum-substrates for PU^A) by defined squeegee procedures, which result in a final, dry layer thickness of around 125 µm for AC^A and of around 40 µm for PU^A and UV^A. For the purpose of life-cycle-analyses, about the half of the produced samples were artificially aged by UV-A-radiation (light wavelength of 351 nm) at a temperature of 50°C without irrigation in accordance with EN 927-6:2006 over a time period of 2000 h.

Project B. In addition to acrylate coatings (AC^B), polypropylene SM-composites (PP^B) were produced and analyzed in project B. The pigmentation of AC^B and PP^B was performed using ten different pigments (carbon black: CB; phthalocyanine green: PC; titania: TD; transparent titania: TT; barium sulfate: BS; transparent iron oxid: TE; quinacridon: RP; aluminum oxide: AO; chromium-antimony-titania: CT; cobalt blue: KB), which varied in particle size, morphology and material. Excepting TD and CT, all pigments consisted of at least one dimension in the nanoscale, i.e. eight of the chosen pigments can be counted among to the definition nano-objects. The AC^B pigment-content varied between 0.7 wt.-% and 15 wt.-% and correlates positively with the pigment size, whereas the pigment-

content of the PP^B was set to 1.0 wt.-%. Injection molding was used for the fabrication of the PP^B-composites, whereas a defined squeegee procedures were performed for applying AC^B on aluminum-substrates. During the artificial weathering procedure a part of the produced samples were exposed to alternating illumination (filtered xenon-arc radiation, 102 min) and irrigation phases (18 min) according to ISO 11341:2004. More detailed information on the samples of project B are summarized in [4].

2.2 Sample treatment

The SC and SM were exposed to a defined mechanical treatment by sanding. For this purpose, a partly enhanced version of a prior developed experimental sanding apparatus [10] was used. The sanding parameter sets of the performed projects are summarized in Table 1.

Parameter		[10] SC	A SC	B SC	SM
sanding area	[cm ²]	13.0	10.4	10.4	10.4
sample speed	[mm/min]	5.0	5.0	5.0	5.0
face velocity	[m/s]	3.9	4.8	4.9	4.9
normal force	[N]	0.5	0.5	0.5	0.5
paper graining	[–]	P600	P600	P1200	P240
rotational velocity	[m/s]	1.83	1.83	1.83	0.73
cutting velocity ratio	[–]	366	366	366	146
cutting power	[W]	1.3	1.3	1.3	0.5

Table 1: Sanding process parameters of project A, project B and previous work [10].

Sanding parameters were chosen in accordance with typical industrial sanding processes as discussed in [10]. In project B, a finer abrasive paper was used for the SC so that the sanding took place exclusively within the weathered region of the samples (cutting depth < 5 µm). As can be gathered from Table 1, the process parameters of the SM differ from the ones of the SC. This is caused by the fact that the sanding process parameters of the SC led for SM to a thermal particle generation, which was indicated by high particle number concentrations (PNC) and average particle sizes below 30 nm. Thus, the sanding parameters of the SM were adjusted according to recommendations for the sanding of polypropylene [11].

2.3 Aerosol characterization

To avoid the entrance of particulate contaminants, the sample treatment was performed in a particle free environment within a laminar flow bench (Model LF-VM-K0615; Steag Laminarflow Prozesstechnik GmbH, Germany). All released particles were captured at the source through a sampling hood, which encapsulated the area of sanding. The exhaust flow from the sanding machine (laden with foreign particles) was directed away from the sampling area to the flow bench outlet.

Several aerosol measurement instruments, like a Condensation Particle Counter (CPC, Model 3022A, TSI Inc., USA), an Electrical Aerosol Detector (EAD, Model 3070A, TSI Inc., USA), an Engine Exhaust Particle Sizer (EEPS, Model 3090, TSI Inc., USA) and an Aerodynamic Particle Sizer (APS, Model 3321, TSI Inc., USA) were combined in a metrological-optimized experimental setup (Figure 1) for the detection of PNC and number-weighted particle size distributions (PSD) in a size-range from 5.6 nm up to 20 µm of the arising aerosols.

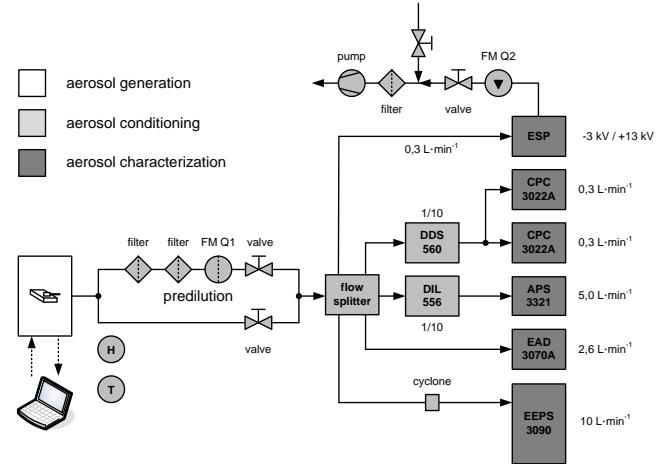


Figure 1. Schematic diagram of the experimental setup.

Caused by the fact that particle-size and particle-concentration measurement devices are not able to distinguish between aerosol particles of different materials, further investigations were carried out. Therefore, electrostatic-deposited (ESP, prototype of model 3089, TSI Inc., USA) swarf particles were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX).

2.4 Experimental procedure

Each sanding process was monitored for a total measurement time of 100 s (including startup and shutdown). At the beginning, the measurement instruments were successively switched on for data recording. 10 s after all instruments were running (lead time for background characterization), the actual sanding process was started for a duration time of 16 s. Afterward, the aerosol analysis was continued for ≥ 30 s to capture all released particles (lag time). Before each analysis, all components of the experimental setup were flushed by compressed air and the sanding tool was equipped with new abrasive paper. The sanding-caused swarf mass was determined by sample weighing within an analytical balance (Model AC210 S, Saturius AG, Germany) with a resolution of 0.1 mg and accuracy of 1.0 mg.

At least six analyses were performed for each sample system (e.g. PU^A, PU^A-ZnO, AC^B, AC^B-TD) and each sample condition (i.e. non-weathered/non-aged or weathered/aged).

3 RESULTS

3.1 Notes on contaminants and repeatability

Particulate contaminants? Different technical measures were performed to avoid any particulate contamination that could lead to artifacts in the release data. Transportation and storage of the artificially aged/weathered samples were realized by a specially developed opaque and airtight sample box to prevent cross-contaminations, to avoid influence by solar radiation and to minimize the contact time with ambient air. As explained in subsection 2.3, the sample treatment was performed under clean room conditions ($\text{PNC} < 0.01 \text{ cm}^{-3}$). The known problem with highly concentrated sander exhaust emissions [e.g. 12] was eliminated by a particle shield for exhaust redirection. Lead time data and also additional investigations, which were performed without contact between rotating sanding tool and sample surface, showed that the technical measures avoid successfully particulate contaminations from the sander exhaust. In addition, these data confirm that the rotating sanding tool releases no particles. Furthermore, no abrasive paper defects (e.g. SiC grain break-out) were observed during performed SEM-analyses on the used abradants. Light microscopic (Axiolab, Carl Zeiss AG, Germany) analyses were performed in order to characterize the sanded area and the cutting depth. Based on the identified coverage ratio of the homogeneous distributed grooves in combination with sanding area geometry and determined swarf mass, sanding-induced cutting depths between $0.3 \mu\text{m}$ - $15 \mu\text{m}$ were calculated for the SC, whereas the SM showed ones between $7 \mu\text{m}$ - $35 \mu\text{m}$. In the case of SC, a contamination by abraded substrate particles can thus be excluded. Beside the sander exhaust emissions, thermal particle generation caused by non-optimal sanding process control can lead to a considerably overestimation of the particle release. Performed thermography analyses (Variocam® Research 270, Jenoptik AG, Germany), carbon dioxide measurements (BINOS®100, Fisher-Rosemount GmbH & Co, Germany) and also the recorded PSD and PNC showed no indication on a thermal particle generation at the sanding conditions given in Table 1.

Repeatability. The repeatability of the release-analyses is affected by various factors like the variability in each sample system (based on e.g. production, aging/weathering, transport, storage) and both random and systematic errors during sample treatment, aerosol conditioning and aerosol analysis. Investigations showed a coefficient of variation between 5 % and 40 %, if the sanding-induced particle release was within the optimum measuring range of the operated instruments (aerosol measurement devices and analytical balance). These values confirm that the repeatability is adequate for systematic analysis on SC und SM regarding the characterization of (nano)-particle release.

3.2 Particle release data

Meaningful and quantitative conclusions about the (nano)-particle release cannot be drawn solely from the measured fractional PNC, because they are influenced by the treatment process parameters and the adjusted analysis conditions. Therefore, different fractional particle release numbers (PRN; $x < 10 \mu\text{m}$, $x \leq 100 \text{ nm}$, $x \geq 1 \mu\text{m}$) were determined and related to treated area taking into account the adjusted dilution ratios and the total volumetric air flow rate [4]. For example, Fig. 2 gives the determined area-specific numbers of released nanoparticles for the different samples.

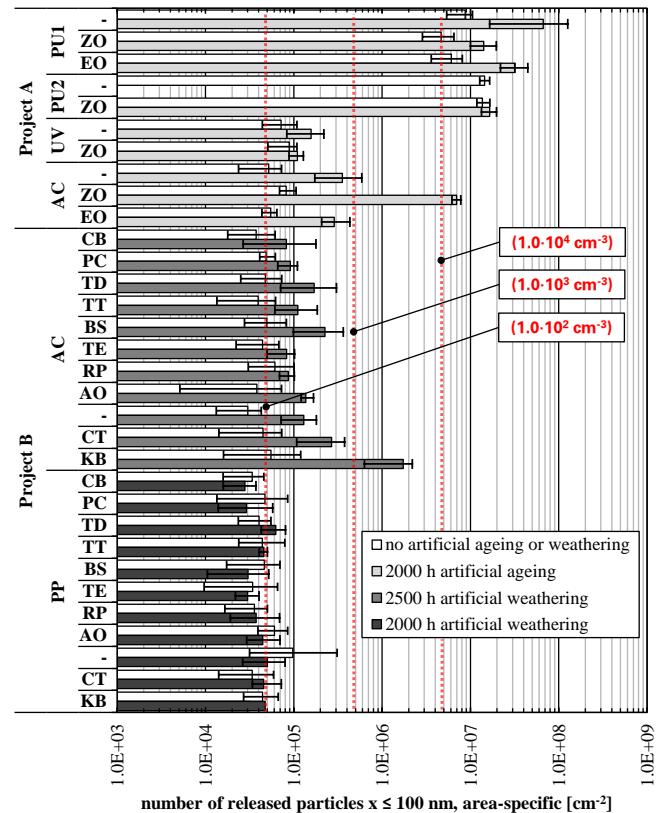


Figure 2. Area-specific number of released nanoparticles; error bars = extrema; dotted lines and values in brackets = process concentration at particle source.

Impact of NPA/NSP admixture. Due to NPA/NSP admixture, no significant impact on the particle release was observed for the SC of project A. This can maybe attributed to the final low mass content of the NPA/NSP in the samples. In contrast, investigations of project B were examined on samples containing pigments with different sizes from the nanoscale up to the submicrometre scale. The pigment size correlates with the pigment mass content in the samples, i.e. the larger the pigments the higher the content. The comparison between the non-pigmented SC and the pigmented ones (for both non-weathered and artificially weathered samples) lead to the conclusion that the pigmentation has a non-negligible impact on the particle release. For ex-

ample, the total particle release ($x < 10 \mu\text{m}$) due to sanding of the non-weathered coatings tends to increase with growing pigment size.

Impact of artificially ageing/weathering. In comparison to their non-aged/non-weathered counterparts, results of both projects showed for all artificially aged/weathered coatings a tendency to higher total particle release ($x < 10 \mu\text{m}$), whereof more than the half showed even a significant increase. In contrast, the SM-data (PP^B) suggest on a reverse effect, i.e. the aged/weathered samples released less particles than the non aged/weathered ones. Considering the area-specific numbers of released particles $x \leq 100 \text{ nm}$ shown in Fig. 1, the artificial ageing/weathering of the SC led also to an increase in the sanding-induced nanoparticle release, whereas no significant differences were observed for the SM samples. Interestingly, some NSP seem to inhibit the nanoparticle release in the aged/weathered state in comparison to the non-pigmented samples. Both, SC and SM, have shown a significant weathering-induced increase in the release of micron particles ($x \geq 1 \mu\text{m}$).

Release of isolated NPA/NSP? Extensive SEM-analyses, which were performed on abrasive paper and electrostatically-precipitated swarf particles, have shown no indication for free isolated NPA/NSP. Independently performed TEM- and EDX-Analyses have shown firmly embedded NPA/NSP (see Fig. 3).

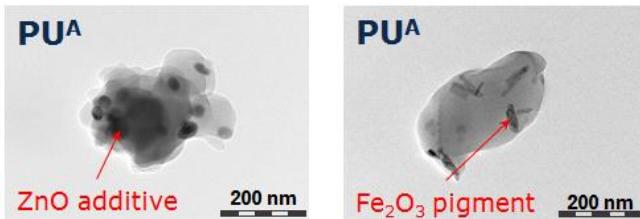


Figure 3. TEM-images of electrostatically precipitated swarf aerosol particles released from artificially aged PU^A.

4 CONCLUSIONS

In the presented studies, systematic analyses on the sanding-induced (nano)-particle release of artificially aged/weathered surface coatings and solid material composites containing nanoscaled pigments or additives were performed using a recently published method [10].

The studies have shown that the (nano)-particle release depends strongly on the applied treatment procedure and that moreover the operation parameters have to be chosen carefully to avoid artifacts. In addition to the treatment procedure, results on the nanoparticle release depend also on the sample material, the sample composition and the sample condition.

The investigations have shown occasional high numbers of released particles, but no free isolated nano-pigments

were observed during performed SEM-, TEM- and EDX-analyses.

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TEM- and EDX-analyses of both studies were performed independently from the own SEM-analyses by Bayer Technology Services GmbH, Leverkusen, Germany.

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