Video Article

Testing of Nanoparticle Release from a Composite Containing Nanomaterial Using a Chamber System

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Abstract

With the rapid development of nanotechnology as one of the most important technologies in the 21st century, interest in the safety of consumer products containing nanomaterials is also increasing. Evaluating the nanomaterial release from products containing nanomaterials is a crucial step in assessing the safety of these products, and has resulted in several international efforts to develop consistent and reliable technologies for standardizing the evaluation of nanomaterial release. In this study, the release of nanomaterials from products containing nanomaterials is evaluated using a chamber system that includes a condensation particle counter, optical particle counter, and sampling ports to collect filter samples for electron microscopy analysis. The proposed chamber system is tested using an abrasor and disc-type nanocomposite material specimens to determine whether the nanomaterial release is repeatable and consistent within an acceptable range. The test results indicate that the total number of particles in each test is within 20% from the average after several trials. The release trends are similar and they show very good repeatability. Therefore, the proposed chamber system can be effectively used for nanomaterial release testing of products containing nanomaterials.

Video Link

The video component of this article can be found at http://www.jove.com/video/54449/

Introduction

Nanomaterial exposure has mostly been studied in relation to workers in workplaces manufacturing, handling, fabricating, and packaging nanomaterials, while consumer exposure has not been studied extensively. A recent analysis of the environmental and health literature database created by the International Council of Nanotechnology (ICON) also indicated that most nanomaterial safety research has focused on hazards (83%) and potential exposure (16%), with the release from nanocomposites, representing consumer exposure, only representing 0.8% [1]. Thus, very little is known about consumer exposure to nanomaterials.

Nanoparticle release has been used to estimate consumer exposure in simulation studies, including the abrasion and weathering of nanocomposites, washing textiles, or dustiness testing methods, such as the rotating drum method, vortex shaking method, and other shaker methods [2-3]. Plus, several international attempts, such as the ILSI (International Life Science Institute) nanorelease and EU NanoReg, have been made to develop technology to understand the release of nanomaterials used in consumer products. The ILSI nanorelease consumer product launched in 2011 represents a life-cycle approach to nanomaterial release from consumer products, where phase 1 involves nanomaterial selection, phase 2 covers evaluation methods, and phase 3 implements interlaboratory studies. Several monographs and publications on the safety of nanomaterials in consumer products have also been published [4-6].

Meanwhile, NanoReg represents a common European approach to the regulatory testing of manufactured nanomaterials and provides a program of methods for use in simulation approaches to nanorelease from consumer products 2. ISO TC 229 is also trying to develop standards relevant to consumer safety and submit a new working item proposal for consumer safety. The OECD WPMN (working party on nanomaterials), especially SG8 (steering group on exposure assessment and exposure mitigation), recently conducted a survey on the direction of future work, especially consumer and environmental exposure assessment. Therefore, in light of these international activities, the Korean Ministries of Trade, Industry and Energy launched a tiered project in 2013 focused on the "Development of technologies for the safety evaluation and standardization of nanomaterials and nanoproducts". Plus, several consumer safety-relevant studies to standardize nanomaterial release from consumer products have also been published [7-8].

An abrasion test is one of the simulation approaches included in the ILSI nanorelease and NanoReg [2-3] for determining the potential emission level of nanoparticles from different commercial composite products. The mass weight loss is deduced based on the difference in the specimen weight before and after abrasion using an abrasor. The nanocomposite sample is abraded at a constant speed, a sampler sucks up the aerosol, and the particles are then analyzed using particle counting devices, such as a Condensation Particle Counter (CPC) or optical particle counter (OPC), and collected on a TEM (transmission electron microscopy) grid or membrane for further visual analysis. However, conducting an abrasion test for nanocomposite materials requires a consistent nanoparticle release, which is difficult due to particle charging as a result of abrasion and when the particle sampling is conducted near the emission point [2-3, 9-11].

Accordingly, this paper presents a chamber system as a new method for evaluating nanomaterial release in the case of abrasion of nanocomposite materials. When compared with other abrasion and simulation tests, the proposed chamber system provides consistent nanoparticle release data in the case of abrasion. Moreover, this new test method has been used widely in the field of indoor air quality and semi-conduct industry as total particle number counting method [12, 13]. Therefore, it is anticipated that the proposed method can be developed into a standardized method for testing nanoparticle release from consumer products containing nanomaterials.

Protocol

1. Preparation of Instruments and Specimens

1. **Abrasor**
   1. Based on an abrasion tester, use an abrasor with one specimen rotation stage (140 mm diameter), two abrasion wheel holders, and a rotation speed of 30 - 80 rpm.
   2. Use a weight to secure the abrasion wheel to the abrasion wheel holder, which also applies load to the test specimen.
   3. Install an additional air inlet to provide better suspension for the abrased particles, as shown in **Figure 3**. Use a 1/8"-diameter tube located 15 mm above and 40 mm away from the center of the test specimen.
2. **Abrasion wheel**
   1. Wrap the abrasion wheel (55 mm diameter, 13 mm thick) with sand paper (100 grit and brand new).
3. **Specimen**
   1. Specimen is a composite containing nanomaterial for abrasion test. To installed at abrasor, the specimen should be prepared with 140 mm diameter.
4. **Chamber**
   1. Use stainless steel for the chamber walls to avoid particle deposition due to electrostatic force. Place the abrasor inside the chamber (volume 1 m^3) (**Table 1**), and locate the air inlet and outlet in the upper and lower part of the chamber, respectively. Use a mixer, consisting of three perforated plates, at the air outlet to achieve a uniformly mixed particle flow.
5. **Neutralizer**
   1. As electro-statically charged particles enhance particle deposition on the chamber walls, use a neutralizer (soft X-ray ionizer) to minimize the charged state of the particles.
6. **Online measuring instruments** [12, 13]
   1. Use a CPC and OPC to measure the particle number concentration and particle size distribution as per manufacturer's instructions.
   2. Install the CPC and OPC at the outlet of the chamber to measure the particle number concentration and particle size distribution.
7. **Particle sampling instruments**
   1. Sample the released particles using a particle sampler containing filter media or a TEM grid to analyze the particle morphology and components.
   2. Install the particle sampler containing filter media or a TEM grid at the outlet of the chamber to analyze the morphology of the release particles.

2. Abrasion Test for Nanoparticle Release Using Chamber System

NOTE: The abrasion test conditions are described in **Table 2**.

1. Locate the abrasor in the center of the chamber.
2. Install the test specimen on the specimen rotation stage of the abrasor.
3. Secure the abrasion wheels in the abrasion wheel holders with a 1,000 g weight to apply load to the test specimen.
4. Locate the neutralizer (soft X-ray ionizer) 28 cm away from the center of the test specimen at a 45° angle, as seen in **Figure 2**, to reduce the electro-static particle deposition on the chamber walls.
   NOTE: The neutralizer removes the electrostatic force by beam exposure. However, since the air inlet and abrasion wheels are located above the specimen rotation stage, this restricts the access of the neutralizer beam to the surface of the test specimen. Therefore, the neutralizer is located diagonally to allow the beam to reach as much of the specimen surface as possible.
5. Operate the blower installed at the outlet of the chamber at a 50 L/min flow rate.
6. Supply 25 L/min additional particle-free suspension air using an air compressor through the additional air inlet.
   NOTE: The particles, which are generated by abrasion, were deposited on surface of the specimen and abrasion wheels, strongly. Therefore, it is hard to measure the abrased particles. The additional air inlet can help to solve this problem to particle suspension.
7. Check the background particle number concentration inside the chamber to reach an average particle number concentration for 1 h of below 1 #/cc using CPC, as described in **Figure 4**.
8. Operate the specimen rotation stage of the abrasor using a step motor that rotates the specimen rotation stage at 72 rpm with 1,000 rotations.
9. Measure and record the released particle number concentration and particle size distribution using the CPC and OPC.

NOTE: The particles released from the nanocomposites are suspended and carried by the air that is being pumped. These suspended particles are eventually transported to the outlet following the airstream. The released particles are then detected by the CPC and OPC at the outlet of the chamber. A CPC and OPC are most frequently used for measuring the particle number concentration, while an OPC can also measure the particle size distribution.

10. Sample the released particles using a particle sampler containing filter media or a TEM grid.
NOTE: The particles released from nanocomposites by abrasion move to the outlet of the chamber following the airstream. At the outlet of the chamber, the released particles can be sampled using a particle sampler. The released particles collected on filter media or a TEM grid can then be analyzed using TEM or SEM (scanning electron microscopy).
11. Stop the measurement and sampling when the particle number concentration reaches below 0.1% of the peak particle number concentration.
12. Save the all data (CPC, OPC) and remove all the samples (test specimens).
13. Use a new specimen and new abrasion wheels for each test, and wash the chamber and abrasor with kimwipes and IPA (iso-propyl alcohol) after each abrasion test to confirm repeatability.

Representative Results

Abrasion Test Repeatability Using Chamber System

The total particle numbers were consistent for 8 abrasion tests, as shown in **Table 3**. The CPC measured an average of 3.67 $\times 10^9$ particles, while the OPC counted an average of 1.98 x 10^9 particles (> 0.3 µm). The deviations were within 20%, which represented a consistent release of particles during abrasion.

Nanorelease from Nanocomposite

As shown in **Figure 5**, Nanocomposites containing CNTs (carbon nanotubes) 0% and 2% showed a circle 40 mm away from the center after abrasion. After abrasion, the original test specimens lost approximately 0.6 g (1.56%) (**Table 4**). The nanocomposite containing CNTs released 12.6% more particles than the control composite, as shown in **Table 5**. Several micrometer particles were sampled on the filter, while a TEM grid was used to sample the nanoscale particles. Most of the particles were torn particles due to abrasion, and FE-SEM (field emission scanning electron microscopy) revealed no free CNT structures from the nanocomposite containing 2% CNTs in the filter samples (**Figure 6**) or mini particle sampler samples after abrasion (**Figure 7**).

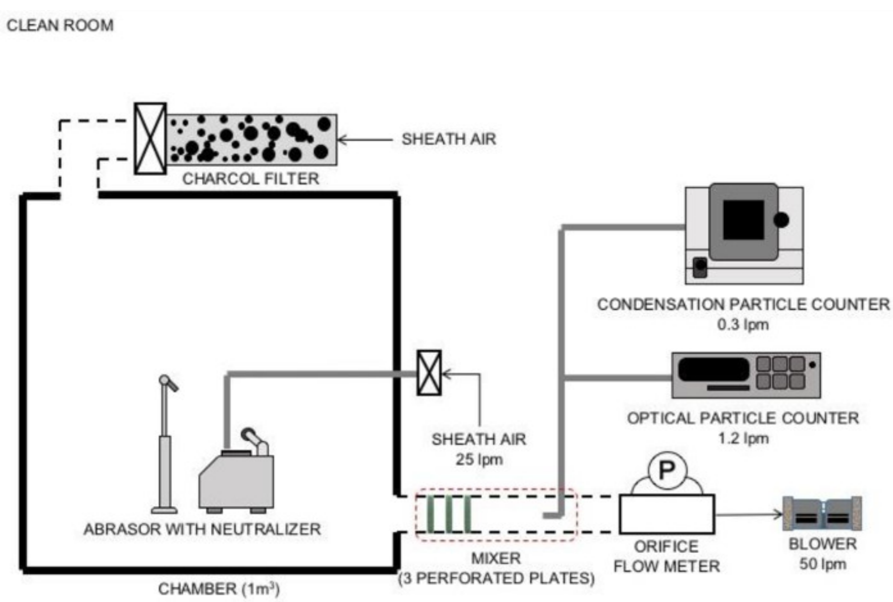

Figure 1. Nanorelease test chamber configuration. This figure shows the configuration of the abrasion test chamber system, and the chamber specifications are presented in **Table 1**. To provide particle-free air to the chamber, a charcoal filter was inserted in the air inlet to inflow sheath air, while a mixer, consisting of three perforated plates, was installed in the outlet to achieve a uniformly mixed particle flow. For air circulation in the chamber, an orifice flow meter and blower were installed at the end of the outlet. A condensation particle counter (CPC) and optical particle counter (OPC) were installed downstream of the mixer to measure the particle number concentration and particle size distribution. Please click here to view a larger version of this figure.

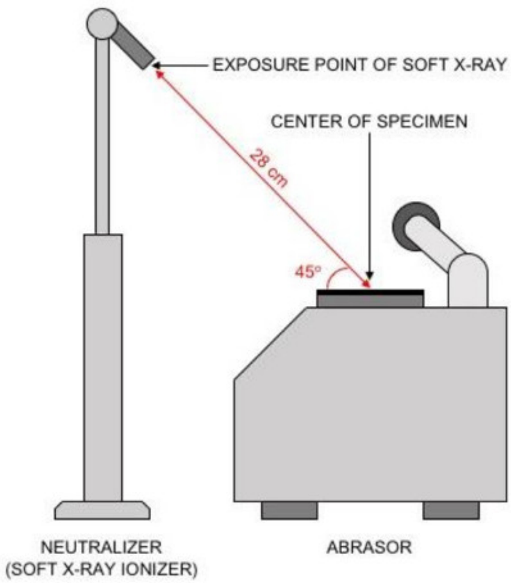

Figure 2. Placement of neutralizer and abrasor. Particles generated by the friction of two different materials will be highly charged. Thus, to reduce the charged particles, a neutralizer (soft X-ray ionizer) was installed. The specifications of the neutralizer are presented in Supplement 1. The neutralizer (soft X-ray ionizer) was located 28 cm away from the center of the test specimen at an angle of 45°. Please click here to view a larger version of this figure.

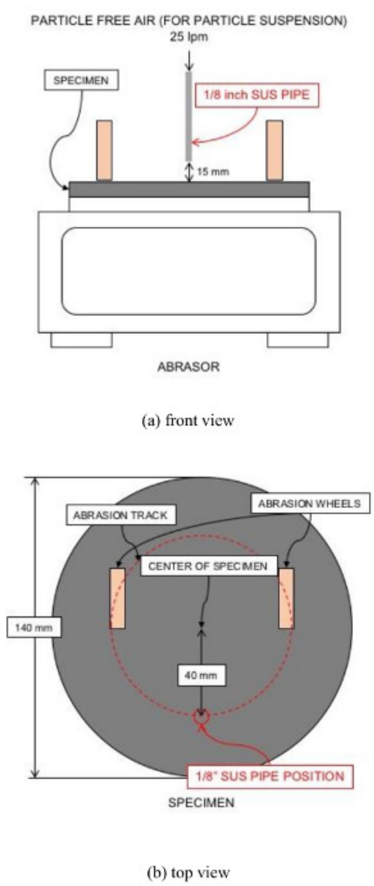

Figure 3. Configuration of additional air inlet: (a) front view (b) top view. For the abrasion test, the abrasor was located in the center of the chamber. To provide better suspension for the abrased particles released from the test specimen, an additional air flow was supplied using a 1/8" tube located 15 mm above and 40 mm away from the center of the test specimen. Please click here to view a larger version of this figure.

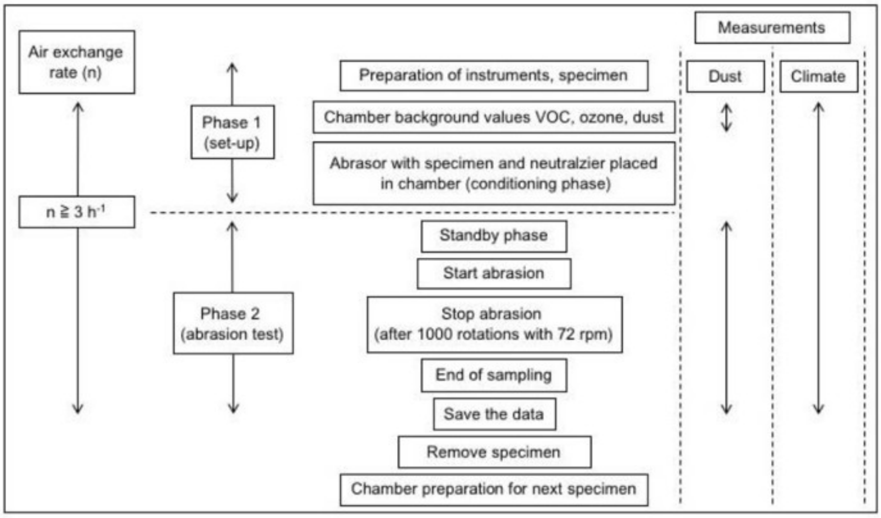

Figure 4. Abrasion test procedure. Before the main experiment, the instruments and test specimens were prepared. The chamber background values, such as the VOC, ozone, and dust, were checked, and then the abrasor with the test specimen and neutralizer were placed in the chamber. For the main test, a zero check was performed in the standby phase by starting and stopping the abrasion. Sampling was performed throughout the abrasion test. After removing the test specimen, the chamber was prepared for the next specimen test. Please click here to view a larger version of this figure.

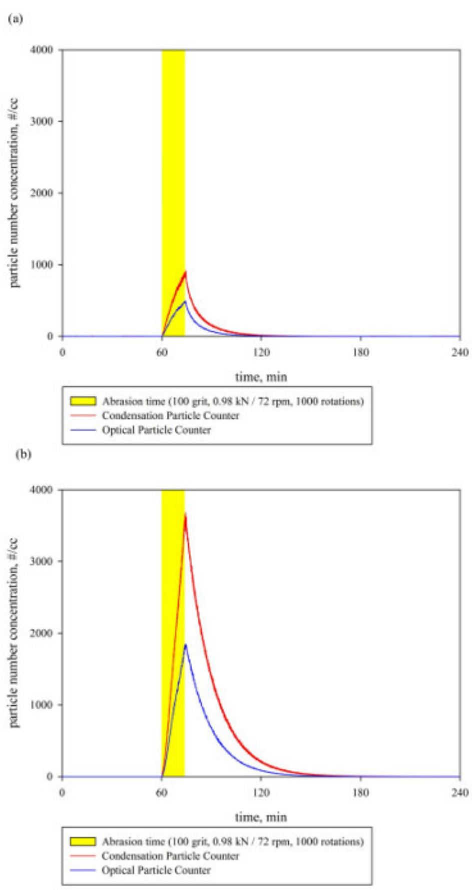

Figure 5. Typical change in particle number concentration during abrasion test. (**a**) Neutralizer off; (**b**) neutralizer on. This figure shows the typical change in the particle number concentration during the abrasion test. During abrasion, the particle number concentration increased, whereas after abrasion, the particle number concentration decreased. (**a**) is the neutralizer-off condition, and (**b**) is neutralizer-on condition. At the neutralizer-on condition, particle number concentration was higher than the off condition. This is because the neutralizer can decrease the particle wall loss by minimize the charged state of the particles. Please click here to view a larger version of this figure.

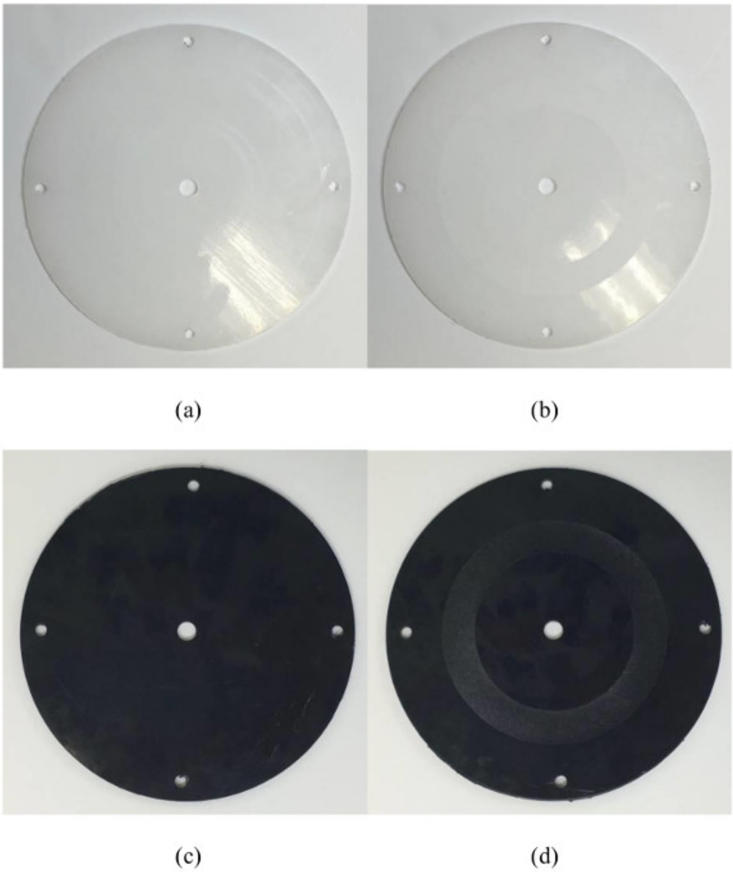

Figure 6. Nanocomposites containing 0% CNTs and 2% CNTs. (**a** & **b**) Not containing CNTs; (**c** & **d**) containing CNTs; (**a** & **c**) before abrasion; (**b** & **d**) after abrasion. Please click here to view a larger version of this figure.

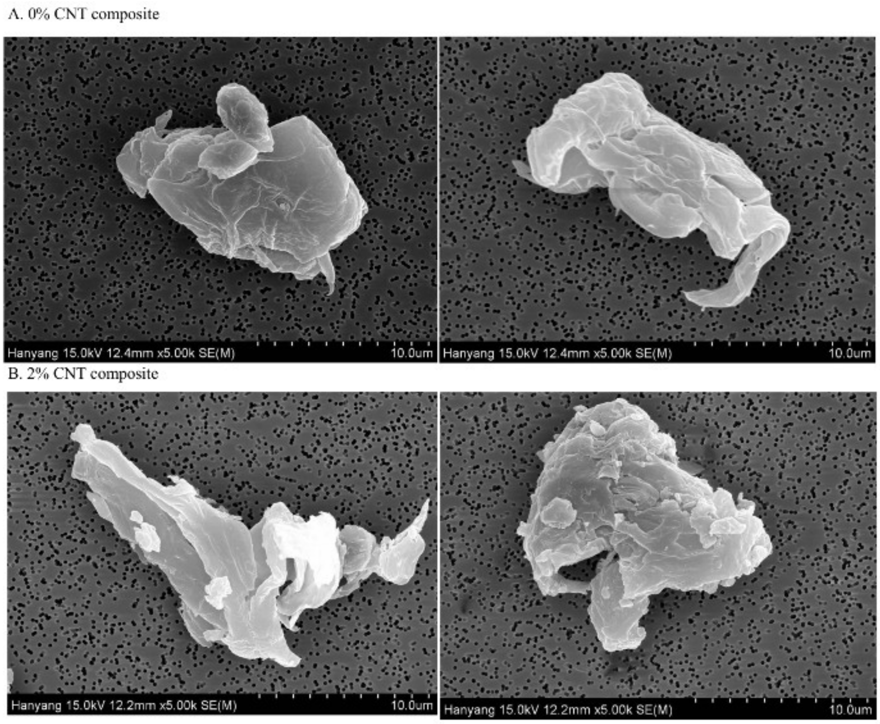

Figure 7. Particles sampled on filter media. The particles released from the composite by abrasion were sampled on the filter and analyzed by FE-SEM. Most of the particles were torn particles due to abrasion, and no free CNT structures were observed. Please click here to view a larger version of this figure.

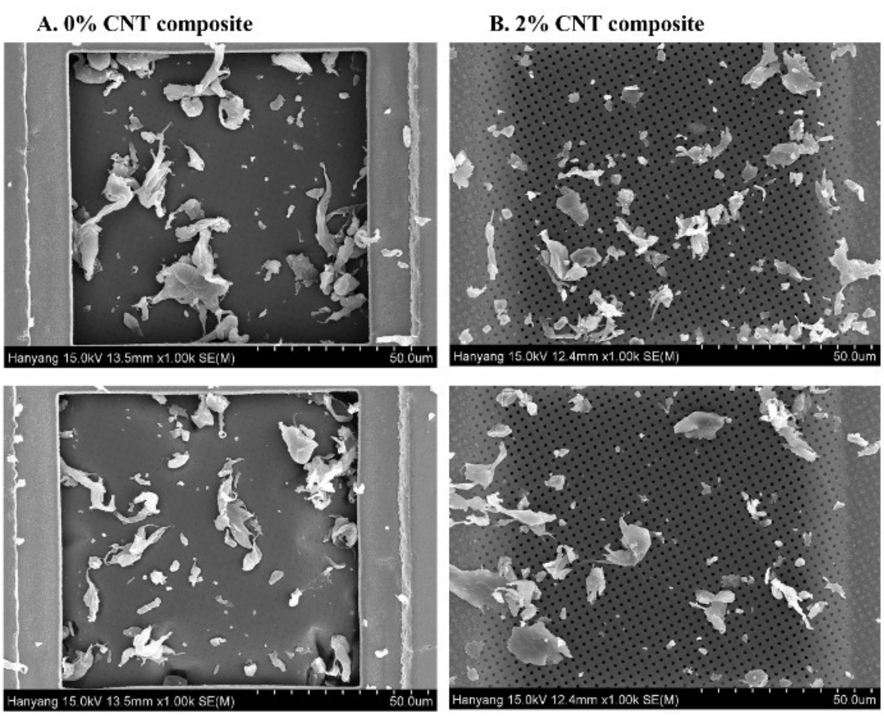

Figure 8. Particles sampled on TEM grid. The particles released from the nanocomposite by abrasion were sampled on the TEM grid and analyzed by FE-SEM. Most of the particles were torn particles due to abrasion, and no free CNT structures were observed. Please click here to view a larger version of this figure.

Dimensions	1,000 mm x 1,000 mm x 1,000 mm (1 m^3), Stainless steel
Blower (with HEPA filter)	200 mm x 200 mm x 200 mm, 909 W
Pressure sensor	Magnehelic, 0 ~ 100 mmH_2O
Filter (chamber inlet)	320 mm x 320 mm x 400 mm, HEPA filter
Charcoal (chamber inlet)	Dia. 90 mm x 260 mm

Table 1. Chamber specifications for abrasion test. HEPA, high efficiency particulate air.

Chamber	**Ventilation**	50 lpm
Abrasor	**Test specimen**	#140 mm, 3 mm thickness
	Abrasion wheels	Sand Paper (100 grit) (brand new)
	Rotation	72 rpm, 1,000 rotations
	Additional air flow rate (for particle suspension)	25 lpm
Neutralizer (soft X-ray ionizer)	**Location**	45 degrees, 28 cm (from center of test specimen)

Table 2. Abrasion test conditions. lpm, liter per min; rpm, revolutions per min.

A. CPC (Condensation Particle Counter)				
	Total particle number [#/cc]			
	Data (x10^9)	Mean ± SD (x10^9)	+20% (x10^9)	-20% (x10^9)
Test #1	2.86	3.67 ± 0.7	4.40	2.94
Test #2	2.61			
Test #3	3.50			
Test #4	4.25			
Test #5	3.87			
Test #6	4.66			
Test #7	3.47			
Test #8	4.17			
B. OPC (Optical Particle Counter)				
	Total particle number [#/cc]			
	Data (x10^9)	Mean ± SD (x10^9)	+20% (x10^9)	-20% (x10^9)
Test #1	1.56	1.98 ± 0.28	2.38	1.58
Test #2	1.81			
Test #3	1.82			
Test #4	2.12			
Test #5	2.05			
Test #6	2.47			
Test #7	1.86			
Test #8	2.15			

Table 3. Total particle number measured using CPC and OPC in 8 abrasion tests. The data are presented as mean and standard deviation of 8 tests.

	Before (g)	**After (g)**	**Weight loss (g) = Before - After**	**Weight loss, %**
CNT (0%)	38.6074	38.0032	0.6042	1.56
CNT (2%)	39.5159	38.9001	0.6158	1.56

Table 4. Weight changes for nanocomposite specimens containing CNTs before and after abrasion.

	Total particle number (#/cc)		Difference (#/cc) = (# of particle CNT 2%) - (# of particle CNT 0%)	
	CPC (x 10^6)	OPC (x 10^6)	CPC (x 10^6)	OPC (x 10^5)
CNT (0%)	8.74	8.37	1.26 (12.6%)	1.6 (1.9%)
CNT (2%)	10	8.53		

Table 5. Total particle number released from nanocomposites after abrasion test.

Discussion

The most critical steps when conducting the nanorelease test from nanocomposite materials using an abrasion test were: 1) using a chamber system made of stainless steel with a neutralizer to remove the electrostatic charge generated by abrasion and reduce the deposition of particles on the chamber walls; 2) supplying additional air to provide better particle suspension; and 3) sampling the released particles and online monitoring using a CPC and OPC from the outlet that contained a mixer consisting of three perforated plates.

The abrasion tester was originally designed to evaluate abrasion resistance based on ISO 7784-1 or ISO 5470-1 [14-15]. Abrasion testers are now widely used to simulate sanding processes and study the abrasion resistances of materials and coatings, and such abrasion methods have been modified to examine the nanoparticle release from nanocomposite materials [9-11]. An abrasion test is also one of the simulation approaches included in the EU NanoReg [2]. However, conducting an abrasion test for nanocomposite materials requires a consistent nanoparticle release, which is difficult due to particle charging as a result of abrasion and when the particle sampling is conducted near the emission point. Therefore, the proposed chamber setting for an abrasion test solves these problems by neutralizing the particles and sampling down-stream of the chamber outlet containing a mixer, thereby achieving a consistent particle release from nanocomposite specimens.

Several attempts have already been made to identify free CNTs released from nanocomposite materials. For example, epoxy-based nanocomposites containing CNTs have been tested for the release of carbon nanotubes using an abrasion process. As a result, transmission electron microscopy (TEM) observation indicated the emission of free-standing individual CNTs and agglomerates during abrasion [16]. In contrast, no free or bundled CNTs were observed in electron microscopic examinations of two different hybrid CNT composites (CNT-carbon composite and CNT-alumina composite) during a machining process, such as dry and wet band-sawing and rotary cutting [17]. Meanwhile, another CNT-epoxy nanocomposite study showed that the particles generated during sanding were mostly micron-sized particles with protruding CNTs and no free CNTs [18]. The current study of nanocomposite abrasion also found no generation of free CNTs when evaluated by extensive electron microscopy. Notwithstanding, the emitted CNT structures will differ depending on many factors, such as the mechanical process, method of manufacturing the nanocomposite, variety of CNT and CNT content in the composite, and resin.

A chamber system has already been used to evaluate the nanorelease from other products containing nanomaterials. For example, to evaluate the risk of silver nanoparticle exposure from antibacterial sprays containing silver nanoparticles, a chamber was successfully used to simulate exposure to silver nanoparticles [7]. Plus, to overcome the difficulties involved with conducting exposure assessment studies in the workplace, simulation studies have been conducted in a chamber to evaluate the extent of silver nanoparticle exposure when working with printed electronic devices using nanosilver ink. In this case, a chamber system containing a printed electronic device and all the sampling instruments described in this paper were shown to be effective for simulation silver nanoparticle exposure evaluation studies [8]. Thus, the proposed chamber method protocol is not only limited to abrasion tests, but can also be applied to other simulation studies to identify nanoparticle release from consumer products containing nanomaterials or nanocomposites.

Therefore, when taken together, the proposed protocol using a chamber system can be used to evaluate the safety of consumer products containing nanomaterials by simulating the handling and manufacturing processes of many products containing nanomaterials. In particular, the consistent results from the proposed chamber system in terms of particle release from products will contribute to evaluating the risk of exposure to nanomaterials released from products. The future intention is to standardize this protocol with extended application to other nanocomposites or consumer products containing nanomaterials in order to characterize human and environmental exposure through the nanomaterial life-cycle and provide a tool for risk assessment.

Disclosures

The authors have nothing to disclose.

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References

1. Froggett, S. J., Clancy, S. F., Boverhof, D. R., & Canady, R. A. A review and perspectives of existing research on the release of nanomaterials from solid nanocomposites. *Part Fibre Toxicol*. **11**, 17 (2014).
2. NanoReg, 2015. *http://nanoreg.eu/images/2015_09_21_NANoREG_Factsheet_D3.3.pdf.* accessed at 11/28/2015. (2015).
3. ILSI (International Life Science Institute) *Nanorelease consumer products. http://www.ilsi.org/ResearchFoundation/RSIA/Pages/NanoRelease1.aspx* (2014), accessed at 12/3/20154. (2014).

4. Kingston, C., Zepp, R., Andrady, A., Boverhof, D., Fehir, R., Hawkins, D., *et al.* Release characteristics of selected carbon nanotube polymer composites. *Carbon*. **68**, 33-57 (2014).
5. Kaiser, D., Stefaniak, A., Scott, K., Nguyen, T., & Schutz, J. Methods for the Measurement of Release of MWCNTs from MWCNT-Polymer Composites, *NIST.* Accessed at 12/3/2015 (2014).
6. Nowack, B., David, RM., Fissan, H., Morris, H., Shatkin, J. A., Stintz, M. *et al.* Potential release scenarios for carbon nanotubes used in composites. *Environ. Int*. **59**, 1-11 (2013).
7. Kim, E., Lee, J. H., Kim, J. K., Lee, G. H., Ahn, K., Park, J.D., *et al.* Case Study on Risk Evaluation of Silver Nanoparticle Exposure from Antibacterial Sprays Containing Silver Nanoparticles. *J of Nanomaterial.* 346586, (2015).
8. Kim, E., Lee, J. H., Kim, J. K., Lee, G. H., Ahn, K., Park, J.D., *et al.* Case study on risk evaluation of printed electronics using nanosilver ink. *Nano Convergence.* in press, (2016).
9. Vorbau, M., Hillemann, L., & Stintz, M. Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings. *J. Aerosol Sci.* 40, 209−217 (2009).
10. Golanski, L., Gaborieau, A., Guiot, A., Uzu, G., Chatenet, J., Tardif, F. Characterization of abrasion-induced nanoparticle release from paints into liquids and air. *J. Phys. Conf. Ser*. **304**, 012062. (2011).
11. Wohlleben, W., Brill, S., Meier, M. W., Mertler, M., Cox, G., Hirth, S. *et al.* On the lifecycle of nanocomposites: Comparing released fragments and their in-vivo hazards from three release mechanisms and four nanocomposites. *Small*. **7**, 2384−2395. (2011).
12. *ECMA-328, Determination of Chemical Emission Rates from Electronic Equipment.* ECMA International, Geneva, Switzerland, (2013), available at *http://www.ecma-international.org/publications/files/ECMA-ST/Ecma-328.pdf*. accessed at 2/11/2016. (2016).
13. SEMI (Semiconductor Equipment and Materials International). *4771A, New Standard: Test Method for Equipment Fan Filter Unit (EFFU) Particle Removal, SEMI.* San Jose, CA. (2013). available at Source: *http://downloads.semi.org/web/wstdsbal.nsf/de4d7939711aeedf8825753e0078317f/70256fe63dab49de8825788e0001d374/$FILE/4771A.pdf*, accessed at 2/11/2016. (2016).
14. *ISO 7784-1, Paints and varnishes -- Determination of resistance to abrasion -- Part 1: Rotating abrasive-paper-covered wheel method.* International Organization for Standardization, Geneva, Switzerland (1997).
15. *ISO 5470-1, Rubber- or plastics-coated fabrics -- Determination of abrasion resistance -- Part 1: Taber abrader.* International Organization for Standardization, Geneva, Switzerland, (1999).
16. Schlagenhauf L., Chu, B. T. T., Buha, J., Nüsch, F, Wang, J. Release of carbon nanotubes from an epoxy-based nanocomposites during an abrasion process. *Enviorn. Sci. Tech*. **46**: 7366-7372 (2012).
17. Bello, D., Wardle, B. L., Yamamoto, N., deVilloria, R. G., Garcia, E. J., Hart, A. J., *et al.* Exposure to nanoscale particles and fibers during machining of hybrid advanced composites containing carbon nanotubes. *J. Nanopart. Res*. **11**, 231−249. (2009).
18. Cena, L. G., Peters, T. M. Characterization and control of airborne particles emitted during production of epoxy/carbon nanotube nanocomposites. *J. Occup. Environ. Hyg*. **8**, 86−92. (2011).