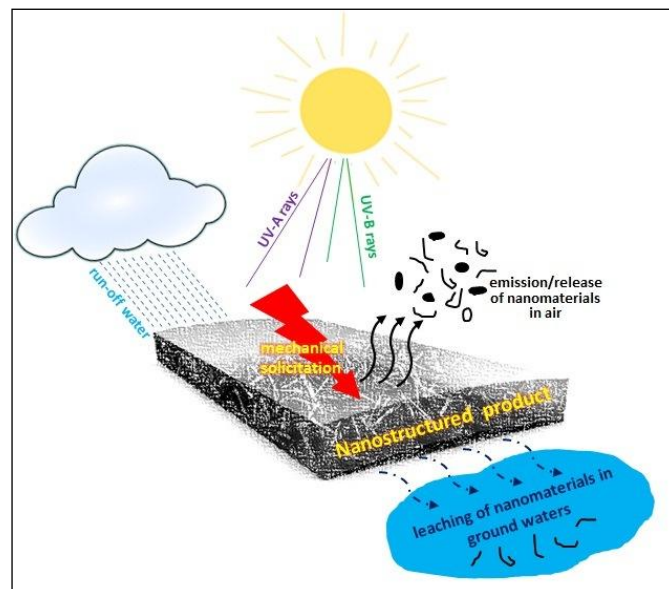


Par Neeraj SHANDILYA

Study of the (Nano) particles emission during mechanical solicitation and environmental weathering of the products

Thèse présentée
pour l'obtention du grade
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Soutenue le 15 janvier 2015

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**THESE POUR L'OBTENTION DU GRADE DE DOCTEUR DE L'UNIVERSITE DE
TECHNOLOGIE DE COMPIEGNE**

**STUDY OF THE (NANO-) PARTICLES EMISSION DURING
MECHANICAL SOLICITATION AND ENVIRONMENTAL
WEATHERING OF THE PRODUCTS**

Présentée par :

Neeraj SHANDILYA

Champ disciplinaire :

Génie des Procédés Industriels et développement durable

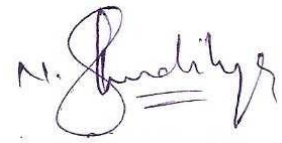
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*Dedicated to my family and past mentors without whom
this milestone would never have been reached !!*

DECLARATION

To the best of my knowledge and belief, this thesis contains no material previously published by any other person except where due acknowledgment has been made. This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

A handwritten signature in purple ink, appearing to read 'N. Shandilya', with a stylized flourish at the end.

Neeraj SHANDILYA

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ABSTRACT

Engineering nanomaterials (ENM) like metal oxide nanoparticles, carbon nanotubes, nanofibers, etc. possess various innovative properties and their industrial use creates new opportunities. However, they also present new risks and uncertainties. There is an ever growing production and use of the products containing these ENM, like nanocomposites or nanocoatings, which result in an increasing number of workers and consumers exposed to ENM upon their emission (in the form of aerosols) from the products containing them. One of the most favored approaches, to minimize this emission, would be a preventive one which would focus on altering the product's material properties during its design phase itself without compromising with any of its added benefits.

This thesis advocates this approach. It attempts to understand the ENM emission phenomenon and its yielding mechanisms on the basis of combined experimental and theoretical approaches. The experimental set-up, developed during this thesis, is equipped with the necessary elements which can (i) seek to reproduce the real life activities on a laboratory scale (ii) identify the emission mechanism (iii) carry out both qualitative as well as quantitative* analysis of the emitted ENM simultaneously. Whilst the mean chosen for applying the mechanical solicitation or stress is an abrasion process, for the environmental weathering, it is an accelerated UV exposure process in the presence of humidity and heat. The results suggest that depending upon 18 material and process properties/parameters, the microscopic entities present on the surface of a product, called asperities, undergo mainly 4 types of removal mechanisms during abrasion. It is these mechanisms that decide the shape, size and the number of the aerosol particles emitted. Moreover, for the given test samples and experimental conditions studied during the thesis, application of the mechanical stresses alone was found to generate the emitted ENM aerosols in which ENM is always embedded inside the product matrix, thus, a representative product element. In such a case, the emitted aerosols comprise of both nanoparticles as well as microparticles. But if the mechanical stresses are coupled with the environmental weathering, then the eventual deterioration of the product, after a certain weathering duration, may lead to the emission of the free ENM aerosols too. All these experimental findings, pertaining to the effect of the mechanical stresses alone, have also been put into the perspective with classical material and mechanics state laws using a predictive analytical model. A close agreement** of the estimated results of this model with the experimentally measured ones has validated its functioning. This model was used to perform a sensitivity analysis on the aforementioned 18 parameters to rank the influence of a 25% variation in each of their values on the particle emission for the given conditions.

Thus, during the present thesis, both experimental and theoretical approaches have been developed to study the emission. Despite the fact that these approaches are perfectible, they can still be used during product design phase for the product to be “nanosafe by design”.

Keywords: Engineering Nanomaterials, Aerosol, Emission, Abrasion, representative product element, Environmental weathering, Analytical model, Simulation, Product design, Nanosafe by design

* Due to the losses of the emitted aerosol particles before they are analyzed for their size and number, the present experimental setup would rather be called semi-quantitative for the moment. These losses are a direct result of the aerosol dynamics, the control of which is beyond the scope of this thesis.

** Obtained after curve fitting and semi-empirical adjustments

RESUME

Les nanomatériaux manufacturés (comme les nanoparticules d'oxydes métalliques, les nanotubes de carbone, les nanofibres etc.) possèdent des propriétés remarquables qui leur confèrent des applications industrielles innovantes. Néanmoins, ces nouveaux matériaux soulèvent des inquiétudes vis à vis de leurs potentiels risques. Ces nanomatériaux manufacturés connaissent une production et une commercialisation croissantes. Par conséquent, de plus en plus de personnes sont potentiellement exposées à ces nanomatériaux (aussi bien les consommateurs que les opérateurs) à travers les aérosols qui pourraient être émis au cours du cycle de vie du matériau. L'une des approches possibles de réduction de risque serait la prévention de l'émission qui consisterait en une conception réfléchie du matériau avec un compromis performance/sûreté.

La thèse présentée ici suit cette approche. Il s'agit de comprendre le phénomène et les mécanismes d'émission des nanomatériaux manufacturés à l'aide d'outils théoriques et expérimentaux. Le dispositif expérimental développé au cours de cette étude vise (i) à reproduire à l'échelle laboratoire des activités en conditions réelles, (ii) à identifier les mécanismes d'émission, et (iii) à mener simultanément des analyses qualitatives et quantitatives* des nanomatériaux manufacturés émis. Pour la sollicitation mécanique, le procédé d'abrasion a été choisi ; quant au vieillissement environnemental, le choix s'est porté sur un procédé d'exposition accélérée aux rayons d'UV en présence d'humidité et de chaleur.

Les résultats suggèrent que les entités microscopiques présentes à la surface d'un matériau (appelées aspérités ou rugosités) subissent globalement 4 types de mécanismes d'enlèvement pendant l'abrasion, suivant la variation de 18 paramètres (liés au matériau et au procédé). Ces mécanismes déterminent la forme, la taille et le nombre de particules de l'aérosol émis. De plus, dans le cas des échantillons testés dans les conditions expérimentales données, il a été observé, lors des essais mécaniques seuls, la génération d'aérosols dans lesquels sont retrouvées des nanomatériaux manufacturés liés à leur matrice. Il s'agit de particules nanométriques et micrométriques. Cependant, dans le cas du couplage abrasion/vieillissement environnemental, après un temps donné de détérioration, il est constaté l'émission de nanomatériaux manufacturés libres, en plus des nanomatériaux manufacturés liés à leur matrice. Les résultats expérimentaux relatifs aux sollicitations mécaniques ont été mis en corrélation avec des lois de mécanique classique utilisant des modèles analytiques. Le modèle utilise en partie des relations semi-empiriques ; après ajustement, on observe une très bonne convergence modèle-expérience. Ce modèle a été utilisé pour réaliser une étude de sensibilité sur les 18 paramètres évoqués précédemment, et ce pour une variation de 25% pour chaque paramètre. Ceci permet d'illustrer la capacité du modèle à hiérarchiser l'influence des différents paramètres sur l'émission de particules, pour des conditions données.

Ainsi, ce travail a permis de développer un ensemble constitué d'une part d'outils expérimentaux et d'autre part d'un modèle. Si cet ensemble est largement perfectible, il permet toutefois d'ores et déjà d'entamer une conception "nanosafe by design".

Keywords: Nanomatériaux manufacturés, Aérosol, Emission, Abrasion, Vieillissement environnemental, Modèle analytique, Simulation, Conception de produits, Nanosafe by design

* Dû à une perte de particules de l'aérosol avant analyse, il serait plus correct de qualifier ces analyses de "semi-quantitatives". Ces pertes sont directement liées à la dynamique de l'aérosol qui n'est pas étudiée dans cette thèse.

LIST OF PUBLICATIONS (in the order of their appearance)

- 1) **Shandilya N.**, Le Bihan O., Morgeneyer, M., A review on the study of the generation of (nano-) particles aerosols during the mechanical solicitation of materials, *Journal of Nanomaterials*, Art. ID 289108, 2014.
- 2) Le Bihan O., **Shandilya N.**, Gheerardyn L., Guillon O., Dore E., Morgeneyer M., Investigation of the Release of Particles from a Nanocoated Product, *Advances in Nanoparticles* 2, 39-44, 2013.
- 3) Morgeneyer M., **Shandilya N.**, Chen Y.-M., Le Bihan O., Use of a modified Taber abrasion apparatus for investigating the complete stress state during abrasion and in-process wear particle aerosol generation, *Chem. Engg. Res. & Design*, 93, 251-256, 2015.
- 4) Le Bihan O., Morgeneyer M., **Shandilya N.**, Aguerre Chariol O., Bressot C., Handbook of Nanosafety- Measurement, Exposure and Toxicology. In: Vogel, U., Savolainen, K., Wu, Q., Van Tongeren, M., Brouwer, D., Berges, M. (eds.) Emission Chambers- A method for nanosafety, Ch. 7, Academic Press, Elsevier Inc., San Diego, 2014
- 5) **Shandilya N.**, Le Bihan O., Morgeneyer M., Effect of the normal load on the release of aerosol wear particles during abrasion, *Tribology Letters* 55, 227-234, 2014.
- 6) **Shandilya N.**, Le Bihan O., Bressot C., Morgeneyer M., Evaluation of the particle aerosolization from n-TiO₂ photocatalytic nanocoatings under abrasion, *Nanomaterials*, Art. ID 185080, 2014
- 7) **Shandilya N.**, Le Bihan O., Bressot C., Morgeneyer M., Emission of Titanium dioxide nanoparticles from building materials to the environment by wear and weather, *Environmental Science & Technology*, 49, 2163-2170, 2015
- 8) **Shandilya N.**, Morgeneyer M., Le Bihan O., First development to model aerosol emission from solid surfaces subjected to mechanical stresses: I. Development and Results, *Journal of Aerosol Science*, 2015 (submitted)
- 9) **Shandilya N.**, Morgeneyer M., Le Bihan O., First development to model aerosol emission from solid surfaces subjected to mechanical stresses: II. Simulation and Sensitivity Analysis, *Journal of Aerosol Science*, 2015 (submitted)

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1. INTRODUCTION

Nanotechnology, which is about controlling matter at near atomic scales to produce unique or enhanced materials, products and devices, is now maturing rapidly. Advances in nanotechnology are driven by rapid commercialization of products containing *Engineered Nanomaterials* (ENM) with remarkable properties. According to the article 18(5) of Regulation 1169/2011, issued by the European Commission, ENM can be defined as any intentionally manufactured material, containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm to 100 nm [1.1]. Moreover, the products containing ENM, either in their solid bulk or on their solid surfaces or in their liquid suspensions, can be termed as *Nanostructured products*. Different types of ENM with different formulations and functionalizations are used in such products according to the nature of application and budget. The products can be in the form of coatings, paints, tiles, house bricks, concrete etc. Apart from inducing the advantages like longer service life and good appearance, they also induce photocatalytic properties to a product. As a result, these nanostructured products can be self-cleaning, air purifying, antibacterial, foul odor destructive and super hydrophilic [1.2].

As far as the research is concerned, one may also find enormous number of publications on the innovations that have been accomplished through nanotechnology. Yet concerns have been raised that the very properties of ENM that make them so attractive could potentially lead to unforeseen health or environmental *hazards* due to the tendency of ENM to get *released* or *emitted* in air in the form of *aerosols* [1.3, 1.4]. An aerosol can be defined as the suspension of solid or liquid particles in the gaseous medium [1.5]. During the use or processing of a nanostructured product, it is subjected to various *mechanical stresses* and *environmental weathering* which facilitate such a release [1.6].

Upon exposure, these aerosols of ENM may interact with human organism through inhalation or dermal contacts and get deposited inside the body [1.7]. Various studies examining the *toxicity* of ENM in cell cultures and animals have shown that size, surface area, surface chemistry, solubility and possibly shape, all play a role in determining the potential for ENM to cause *harm* [1.7]. It is generally accepted that, in principle, some ENM may have the potential to cause harm to people and the environment.

Without any thorough understanding and with ongoing unprecedented use of nanostructured products, people producing and using nanomaterials could develop unanticipated health related complications arising from their *exposure*; public confidence in nanotechnologies could be reduced through real or perceived dangers; and fears of litigation may make nanotechnologies less attractive to investors and the insurance industry [1.8].

Nevertheless, this problem has now started getting attention by the researchers and has been highlighted recently by various research units throughout the world [1.6, 1.9-1.15]. One of the most persistent approaches in the contemporary research has been to select certain nanostructured products and subject them to various mechanical stresses and weathering. The eventual release of ENM is characterized experimentally in terms of their *number concentrations*, *size distributions*, *elemental compositions* and *shapes* [1.5]. To better understand, number concentration of ENM can be defined as the number of ENM present in unit cubic centimeter of air [1.5]. On the same note, size distribution of ENM is the

relationship expressing the quantity of an ENM property (usually number and mass concentrations) associated with particles in a given size range [1.5].

This approach is important to develop a database of different ENM release tendencies and order or group them. However, it is not *preemptive*, especially when there is a large scale deployment of nanostructured products. Such an approach of carrying out tests for each type of product is tiresome, insufficient and non-effective.

Therefore, a preventive approach which is:

- based upon the identification of underlying ENM release mechanisms
- based upon the identification of the alternations in material properties with ENM addition
- able to predict the quantity of ENM emission

is required. Such an approach shall be highly valuable in developing the products which are low emissive with respect to ENM emission or “*nanosafe by design*”.

The present thesis is motivated from the fact that understanding the release mechanisms of the ENM during wear and weathering of the materials is important due to various potential health aspects. Therefore, for the present thesis, we decide to study the ENM emission from various nanostructured and traditional products when they are subjected to mechanical stresses and environmental weathering.

In order to do so, following five aims are defined for the thesis:

1. To suggest a suitable mechanical process that can reproduce the real life mechanical stresses and aid to study the ENM emission under the effect of these stresses
2. To identify the parameters which play a key role during the aerosol particles emission
3. To develop an experimental set-up that can produce reproducible results, measure and control the identified key parameters
4. To study the effect of mechanical stresses and environmental weathering couple on the aerosol particles emission from commercial nanostructured products
5. To develop a first generation analytical model that can quantitatively predict the aerosol particles which get generated during mechanical stress application of an isotropic material

As it is clear from these aims, the research required for this thesis is not limited to a certain discipline but it is rather multidisciplinary. It spans over the study in the fields of Material Physics, Material Fracture Mechanics, Tribology and Aerosol Physics. Moreover, utmost care is taken during the planning of this thesis so that it doesn't remain limited to either of the experimental approach or theoretical approach but the combination of the two.

This manuscript is organized in the same order as that of the five abovementioned aims. Starting with presenting the state of the art of the subject, an overview of all the contextual scientific studies is provided in section 2. In this section, the need for the multidisciplinary in the approach is underlined in order to better understand the ENM emission mechanisms.

The section 3 provides information on different types of the characterization techniques that were used during the course of this thesis and various preliminary studies that were carried out on traditional materials (material with no ENM in the matrix) in order to further enhance our understanding and identify the key parameters in the particle emission mechanism.

Based on the understanding developed in the sections 2 and 3, section 4 spots light upon the experimental set-up that was developed during this study. This experimental set-up was developed in such a way that it should allow to measure the parameters that were found to be decisive in ENM emission mechanisms.

Once the emission mechanism is understood and an experimental set-up has been developed, it was the time to test the nanostructured products containing ENM. This aspect is dealt in the section 5 where, through the means of three different case studies on two nanostructured products, the effects of the application of the mechanical stresses and the environmental weathering on the ENM emission are shown.

In the section 6, an analytical model is presented. This model puts the experimental data (generated in the sections 3, 4 and 5) in perspective with the classical material and mechanics state laws. All the identified key parameters (found in section 3) have been simulated and their analytical relations with the emission have been established using this model.

At the end, a section on the discussions and general conclusions is provided to summarize the key findings of the thesis and put them in perspective with the tasks to follow.

-
- [1.1] Potocnick J., European Commission Recommendation on the definition of nanomaterial, 2011/696/EU, Oct 2011
 - [1.2] Torgal F.P., Jalali S., Eco-efficient construction and building materials. *Constr. Build. Mater.* 25, 582-590, 2011
 - [1.3] Oberdorster G., Oberdorster E. and Oberdorster J., Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles, *Environmental Health Perspectives* 113, 823-839, 2005
 - [1.4] Houdy P., Lahmani M. and Marano F., *Nanoethics and Nanotoxicology*, Springer, Heidelberg, Germany, 1st edition, 2011
 - [1.5] Kulkarni P., Baron P. A. and Willeke K., *Aerosol Measurement: Principle, Techniques and Applications*, John Wiley and Sons, Hoboken, NJ, USA, 3rd edition, 2011
 - [1.6] Hsu L.Y. and Chein H.M., Evaluation of nanoparticle emission for TiO₂ nanopowder coating materials, *Nanoparticle Research* 9, 157–163, 2007

- [1.7] Maynard A.D., Safe handling of nanotechnology, *Nature* 444, 267-269, 2006
- [1.8] Shatkin J.A., Abbott L.C., Bradley A.E., Canady R.A., Guidotti T., Kulinowski K.M., Löfstedt R.E., Louis G., MacDonell M., Maynard A.D., Paoli G., Sheremeta L., Walker N., White R., Williams R., Nano risk analysis: advancing the science for nanomaterials risk management, *Risk Analysis* 30, 1680-7, 2011
- [1.9] Göhler D., Nogowski A., Fiala P., Stintz M., Nanoparticle release from nanocomposites due to mechanical treatment at two stages of the life-cycle, *Phys Conf Ser* 429, 2013, DOI: 10.1088/1742-6596/429/1/012045.
- [1.10] Allen N.S., Edge M., Corrales T., Childs A., Liauw C.M., Catalina F., Peinado C., Minihan A., Aldcroft D., Ageing and stabilisation of filled polymers: an overview, *Polym Degrad Stabil* 61, 183-199, 2004
- [1.11] Allen N.S., Edge M., Ortega A., Sandoval G., Liauw C.M., Verran J., Stratton J., McIntyre R.B., Degradation and stabilisation of polymers and coatings: nano versus pigmentary titania particles, *Polym Degrad Stabil* 85, 927-946, 2004
- [1.12] Al-Kattan A., Wichser A., Vonbank R., Brunner S., Ulrich A., Zuind S., Nowack B., Release of TiO₂ from paints containing pigment-TiO₂ or nano-TiO₂ by weathering. *Env Sci Process Impact* 15, 2186-2193, 2013
- [1.13] Kaegi R., Ulrich A., Sinnet B., Vonbank R., Wichser A., Zuleeg S., Simmler H., Brunner S., Vonmont H., Burkhardt M., Boller M., Synthetic TiO₂ nanoparticle emission from exterior facades into the aquatic environment. *Environ Pollut* 156, 233- 239, 2008
- [1.14] Hirth S., Cena L., Cox G., Tomovic Z., Peters T., Wohlleben W., Scenarios and methods that induce protruding or released CNTs after degradation of nanocomposite materials, *Nanopart Res* 15 1504-1518, 2013
- [1.15] 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* 7, 2384-2395, 2011

2. STATE OF THE ART

The present section aims to present the forefront of the research state as far as the aerosol particles emission during stress applications is concerned. It derives its significance from the fact that the advances in adding ENM to various types of matrices have somehow surpassed the research related to the identification of potential hazards associated with exposure to ENM because understanding and preventing risk often has a low priority in the competitive world of research funding.

This section reviews various contextual studies in the field of tribology and the aerosol physics that have been carried out on the thematic of understanding what is known about the particles emission from various traditional and nanostructured products when they are subjected to the mechanical stresses coupled with environmental weathering.

An article, entitled “A review on the study of the generation of (nano-) particles aerosols during the mechanical solicitation of materials”, is presented here for this purpose. It is divided in two principle parts which deal with the experimental and theoretical states of the present day knowledge on this subject respectively. In addition, different types of the characterization techniques which identify the number, size, shape and chemical composition of the emitted particles are also shown.

The data gathered from the studies based on these characterization techniques highlight that the release of ENM from nanostructured products may take multiple forms and that additional research and guidance would be beneficial, allowing for more consistent characterization of the release potential of ENM. In addition, these data support calls for method validation and standardization, as well as understanding how laboratory released scenarios relate to the real world conditions.

Even though limited, the review of the research publications and databases based on the data generated on potential ENM hazards or exposures reveals that relatively a little attention has been focused on understanding the potential and conditions for release of ENM from the nanostructured products.

The major factors that are considered to have a potential to affect the properties and release mechanisms of the emitted particles are also enlisted and explained in this article. They are the contact surface conditions, contact stress conditions, friction heat dissipation and nature of the materials.

Hence, during our study we learned that the following challenges are considered to still remain to tackle in order to better understand the risk related to the exposure of the ENM:

1. To evaluate the impact of ENM emission during their use in real life conditions where they are subjected to both mechanical stresses and environmental weathering
2. To develop instruments that could quantify and separate the emitted ENM under study from background noise on an industrial scale
3. To identify and understand various underlying physical phenomena that lead to the ENM release
4. To develop models for predicting the ENM release in the environment

Using this study, we were able to develop the state of the art of the concerned subject as well as our research strategy which shall automatically become clearer later.

Review Article

A Review on the Study of the Generation of (Nano)particles Aerosols during the Mechanical Solicitation of Materials

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This paper focuses on presenting the forefront of the interdisciplinary studies conceived towards the generation of the wear particles aerosol when materials are subjected to mechanical stresses. Various wear mechanisms and instrumentation involved during stress application and aerosolization of wear particles, as well as particles characterization, measurement, and modeling techniques are presented through the investigation of a series of contextual works which are emphasized on the identification of these aspects. The review is motivated from the fact that understanding mechanisms involved in wear-induced particle generation, both at nano- and at microscale, is important for many applications that involve surfaces sliding over each other due to various potential health aspects. An attempt has been made to explain how the information based on this broad spectrum of subjects discovered in this contribution can be used and improved in order to produce a more resilient, rational, and versatile knowledge base which has been found lacking in the present literature during its survey. The area of study is highly multidisciplinary since it involves aerosol, particle, and material sciences.

1. The Problem Formulation

Advances in nanotechnology are driven by rapid commercialization of products containing nanomaterials with remarkable properties. This is reflected in the enormous number of publications on nanotechnology. These nanomaterials may have a tendency to get released in air in the form of *particle aerosol*. Particle aerosol is the suspension of solid or liquid particles in the gaseous medium. It is generally formed by the disintegration of liquids or solids into finer constituents. In [1], authors have explained comprehensively how the particles, after being generated, get suspended in air to form an aerosol along with the behavior associated with their different structures. Various physical phenomena (e.g., dispersion, coagulation, sedimentation, etc.) are also explained which guide their size evolution. When the number of publications on characterization of this particle aerosol in the workplaces was enquired through the means of this study, it was found that it is comparatively much smaller. In

spite of this, the fact cannot be denied that the overwhelming use of manufactured nanomaterials (MNM) in contemporary applications has brought potential risks to the workers and consumers due to their release in air during their use. Upon exposure, these nanomaterials may interact with human organism through inhalation or dermal contacts and get deposited inside the body. In fact, their interaction modes with human body and potential hazards associated with them form the basis of another newly emerging field of study called *nanotoxicology* [2, 3]. This problem has now started getting attention by the researchers and has been highlighted recently by various research units throughout the world. In one of these researches on industrial production and professional application of manufactured nanomaterials-enabled end products in Dutch industries [4], the researchers have found that 76% of the companies, having potential risks related to working with MNM, do not have a specific point of interest towards the exposure controls, thus demonstrating a lack of awareness. The total number of workers potentially

exposed to MNM during the production or application of MNM-enabled end products is estimated to be approximately 3,000 in The Netherlands. A literature review by European Agency for Safety and Health at Work (EU-OSHA) on workplace exposure to nanoparticles [5], has mentioned that the available information on the generation and measurement technology of the nanomaterials at workplaces is currently superficial. During another study on the sources of generation of nanoparticles aerosols, [6] has realized the lack of a “rational science-based approach” to minimize their generation and supported the continued study with appropriate industrial development. The Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR) [7] has stressed in a scientific report on an approach of case by case basis for the assessment of nanoparticles presence. Insufficient knowledge and data concerning nanoparticles characterization and their detection and measurement have also been indicated. The research report by “L’Institut de Recherche Robert-Sauvé en Santé et en Sécurité du Travail” (IRSST) [8] favors a preventive approach aimed at minimizing occupational exposure to nanoparticles when their risk assessment cannot be established precisely. They propose a step-by-step approach, followed by some examples of applications in industry or research. In a document issued by National Institute for Occupational Safety and Health (NIOSH) and Centers for Disease Control and Prevention (CDC) on the approaches to safe nanotechnology [9], the authors have identified workplace tasks in which there is a huge risk of exposure to nanomaterials. Some of them are generation of nanoparticles in nonenclosed systems; handling tasks (weighing, blending, spraying, etc.) of nanomaterials; maintenance on equipment and processes used to produce or fabricate nanomaterials and the cleaning-up of spills and waste material containing nanomaterials; and cleaning of dust collection systems used to capture nanoparticles; machining, sanding, drilling, or other mechanical disruptions of materials containing nanoparticles. One should note that all these activities involve the application of stresses on a surface.

From the outcomes of aforementioned researches or surveys, it is clear that the manufactured nanomaterials may pose a serious problem if not assessed properly. Their generation and characterization techniques are still underdeveloped. Therefore, this work presents a state of the art of such an aspect. It focuses on the works that may contribute towards the development of a base explaining the (nano)particle release mechanisms and principles conceived up to date. It further discusses the methods being adopted towards the study of their release, characterization, and modeling. This paper targets all the stakeholders associated with production or processing or use of nanomaterials-academics, industries, and government research organizations. The paper is organized as follows. Section 2 deals with the experimental state of the present knowledge, thereby presenting different solicitation methods and characterization techniques; Section 3 structures the theoretical base present which could prove to be useful while modeling; Section 4 discusses various outcomes of this study and projects a prospective direction towards the improvement of the knowledge base

on the (nano)particles release. An annexure is also provided which further elaborates the description of the instruments that have been used to provide solicitation and have been mentioned in Section 2. The authors have tried to present an exhaustive image of the state of the art as far as possible but further suggestions from readers towards its improvement would be welcomed.

2. Experimental State

2.1. Contextual Tribological Studies Conceived. The study of the wear mechanisms started with the study of the development of the force of friction during a relative displacement between two surfaces. It has been carefully discussed how a consideration of the deformation of the two bodies may be used to explain friction [18]. Bowden and Tabor have shown that the interaction between the two bodies in the area of contact, where they come very close together on an atomic scale, is so strong that the application of a tangential force tending to slide two normally loaded bodies over each other nearly always produces deformation and wear in the bodies themselves, rather than slip in the original interface. The process of continuous sliding theoretically has been examined and showed the importance of the strength of the surface interaction [19]. Verkhovskii seems to have been the first to point out that very high pressures would occur in the small regions of contact of rough bodies and that these regions would therefore be in a wear state. The contact of the rough bodies at atomic scale can be understood better if the surfaces are considered to be composed of asperities. The generation of the particles can be directly associated with the rupture of these asperities. The asperities have been used to explain a critical limit of the load existing during the abrasion of two bodies [20]. If the load increases above this critical limit, the softer material of the two sliding bodies would experience continuous incremental deformation and hence wearing starts.

This critical limit was further investigated by assuming two particular geometries for asperities: spherically tipped and cylindrical [20]. They found that the critical limit can be influenced by the machining processes used to prepare the harder surface, at least in so far that this leaves its mark on the surface topography. However, such a shape assumption for the asperities yields an isotropic deformation of the asperities because of their symmetrical shape. Considering an anisotropic deformation of the asperities, [21] presented a unique study for a *microslip* between a flat smooth surface and a flat rough surface covered with uniformly distributed ellipsoidal elastic bodies. *Microslip* is a small relative tangential displacement in a contacting area at an interface when the remainder of the interface in the contacting area is not relatively displaced tangentially [22]. Reference [23] presented the concept of input wear energy during the subsection of a material to mechanical stresses which they demonstrated to be proportional to the number of released aerosols of wear particles.

There have been three wear mechanisms explained and considered to be responsible for material removal during abrasion: ploughing, cutting, and wedge formation [24].

These mechanisms were shown to be functions of degree of penetration of one body inside the other, which in turn depends on the normal load, true area of contact, and the hardness of two materials: $D_p = R(\pi H_v/2W)^{1/2} - ((\pi H_v/2W)R^2 - 1)^{1/2}$, where D_p is the degree of penetration, R is the radius of the tip of the penetrator, H_v is the hardness of the specimen, and W is the normal load.

2.2. Identification of Solicitation Methods Used. A material starts wearing when it is exposed to a certain degree of solicitation which can be done in a number of forms: mechanical, thermal, UV, stress, and so forth. The solicitation methods can be broadly classified in two categories: high energy and low energy input.

2.2.1. High Energy Input. In this category, range of mechanical devices can be included which operate on high transmission power and thus high input and output. This includes grinders and sanders. These types of devices are mainly used in the material processing sites. A review of various significant solicitation studies has already been shown in [23]. In the present work, the studies which remained excluded, but inevitable, are mentioned. While grinding beryllium ceramic, [25] found a domination of the particles <100 nm in the number weighted aerosol size distribution generated. Reference [26] has demonstrated that dry paint scrapping and sanding can lead to substantial particle number concentrations below 1 μm . Reference [10] used high speed grinding to verify the mechanical generation of ultrafine aerosol particles. They found a particle size range of 4.22 nm to 20.5 μm . The substrates selected for the study were steel, aluminum, PTFE, hardwood, granite, and clay ceramic. They concluded that the ultrafine particles do have the potential to form a significant component of a grinding aerosol for a number of substrates. Reference [11] used an abrasion process for applying the mechanical stress on the surface of a cotton fabric sample covered with silica nanoparticles. Reference [27] investigated the potential size distributions of sanding dust released from paints produced with and without nanoparticles. Dust emissions from sanding generated the particles in various size modes in which the number concentrations varied considerably in between the nanoparticles doped and reference paint. Reference [12] subjected a semimetallic brake lining to full scale automotive brake dynamometer tests. They found that the released wear debris has different sizes and shapes at different values of applied pressure, sliding velocity, and temperature. Reference [28] reported 35% of the wear debris to be airborne while [29] reported it up to 50%.

References [13, 14, 30, 31] investigated the wear resistance of the components using Taber test. The primary measurement result was the mass loss which is a measure of the wear resistance. Reference [31] compared the wear resistance of the cutting tools for an interrupted cut machine by means of Taber test. Reference [13] developed a sensitive test method for the quantification of the particle release from coated surfaces into air by a defined stress, comparable to the domestic use. However, the total number of generated sub-micronic or nanoparticles was extremely low and lies below the statistic significance threshold. During the abrasion of an

epoxy-carbon nanotube nanocomposite [14], the measured particle concentrations of the particles lying between 20 nm and 800 nm were between 8000 and 20000 particles/ cm^3 , whereas, [32] emphasized on the design of nanocomposites with SiO_2 and TiO_2 nanoparticles for the hazard reduction extending to the full nanocomposite life cycle. It has been pointed out by [33, 34] that, if TiO_2 nanoparticles are used in nanocomposites with organic polymers, there can be a substantial increase in the degradability under solar or UV irradiation. Thermal degradation may also be enhanced by the incorporation of nanoparticles. Reference [35] provided evidence that TiO_2 nanoparticles used in polymeric wall paints are detached from new and aged facade paints by natural weathering. Reference [15] studied the effect of Taber abrading, sanding, and UV radiations on the thermoplastic and cementitious nanocomposite materials. They confirmed the phenomenon of *chalking*, that is, release of pigments from weathered paints from the thermoplastic composites under the UV radiations. In a similar work [36], release of free CNTs was not detected under any condition using several detection methods during the abrasion and machining of a CNT-TPU composite. During their study of nanoparticle emission of TiO_2 nanopowder coated on different substrates including wood, polymer, and tile, [37] found that the tile coated with TiO_2 nanopowder produces highest particle emission (no. 22/ cm^3 at 55 nm) due to nanopowder separation during the simulation process done by using a UV light, a fan, and a rubber knife in order to simulate the sun light, wind, and human contacting conditions. Also, the UV light was shown to increase the release of particle below 200 nm from TiO_2 nanopowder coating materials. Reference [38] reported the influence of nanoclay on mechanical drilling of PA6 composites, in terms of dust generation. They found a total particle concentration of 20,000 cm^{-3} over a particle size range of 5 to 512 nm. During a sanding test of a nanocoated piston cap, [23] found that the total number concentration of the released particles was dominated by the nanoparticles with a mean diameter size of 35 nm. This finding was found to be coherent with [27] and Göhler et al. [39].

2.2.2. Handling. The handling of materials, that is, storing, conveying, filling, and mixing, leads to dust liberation. This capability of generating dust is described as dustiness. This type of release of particles is characterized by low energy input. However, the multitude of dust generation varies from process to process. For example the particle generation associated with daily activities of solid material handling may differ from handling of disperse particle systems. Reference [23] demonstrated an insignificant particle release [40] during the conventional handling operations like extraction of a part from its bag, bag agitation, displacement of the part with some small physical impacts, and rubbing with gloves. On the contrary, the dust liberation property of disperse particle systems depends on a multitude of variables and also on the method and intensity of stressing. During an investigation of TiO_2 and SiO_2 powders in free drop conditions, [41] demonstrated a release of nanoparticles of 10 mg/m^3 and 40 mg/m^3 for TiO_2 and SiO_2 , respectively. The SWCNT agitating principle of [42, 43] in a centrifuge tube has also

been used by [44] to characterize the amount, particle size distribution, and morphology from different nanostructured powders including TiO_2 and ZnO and carbon materials like SWCNT, MWCNT, and fullerenes. To improve the aerosolization process of CNTs, [45] agitated the sieve plate of the fluidized bed by a shaker. The results showed a considerable release of CNTs with material specific fractions of particles/agglomerates in the nanometer size range.

2.3. Characterization

2.3.1. Mass or Number Characterization. Mass or number characterization means the characterization of the particles release in terms of their number or mass. Such characterization techniques require the detection of the particle concentration and the number size distribution. Reference [46] has already presented a comprehensive list of various existing measurement and sampling devices for airborne nanoscale materials used in workplace exposure studies. In order to present a state of the art of this aspect, Table 1 presents some of the techniques which are at the instrumentation forefront. Reference [47] did an investigation on the production of dust by hand sanders when used without dust extraction, with integral dust extraction, and with external dust extraction. The apparatus used for the measurement was designed to carry out sanding in a repeatable manner, simulating normal working practice. The first well-recognized study on the particles size distributions of airborne particles released during the machining of the materials was done by [10]. As demonstrated by Figure 1, they characterized the particles size distribution over particles sizes ranging from 4.2 nm to 20.5 μm , produced from the high speed grinding of a variety of materials, by using a Condensation Particle Counter (CPC 3022A TSI) Scanning Mobility Particle Sizer (SMPS) in conjunction with a Differential Mobility Analyzer (DMA 3085 TSI), and Aerodynamic Particle Sizer (APS 3320 TSI). Prior to feeding these instruments, the flow was being passed through a stainless steel chamber acting as an emission chamber [48] for background particles free air. Reference [27] investigated the particle size distributions of sanding dust released from paints produced with and without engineered nanoparticles. They characterized the emitted particles in terms of number size distribution as well as surface area and mass size distribution. The particle size distribution was measured from the chamber using an APS Model 3321 TSI, a TSI diluter model 3302A due to high particle concentrations, and a Fast Scanning Mobility Sizer (FMPS 3091 TSI). Reference [11] used SMPS Grimm 5.5–300 and CPC Grimm 5.403 to characterize the concentration and number size distribution for the nanoparticles emitted during the Taber abrasion of a fabric piece made of a PET layer coated with an additional PVC layer containing nanoclays.

Figure 2 shows their findings. Reference [13] combined the methodology adopted by [11] for abrasion and [10] for the characterization of the particles released during the abrasion of the fiberboard surfaces coated with two different mixed batches polyurethane. A similar approach was again adopted during the Taber abrasion of epoxy-carbon nanotube nanocomposites [14].

It is worth mentioning that the present work does not include the studies which have been discussed in [23]. Therefore, the readers are encouraged to refer the same [23] in order to have more comprehensive idea.

2.3.2. Microscopy. The microscopy of the particle released during the solicitation process can be done offline by capturing and collecting them for analysis, that is, sampling [49]. Microscopic analysis may help in determining the state of existence of the particles in air when released from the surface which may be agglomeration or dispersion. Morphology of the particles can also be observed directly which may further help in controlling the solicitation parameters according to the intended morphology of the particles. If the solicitation of a two-phase material (composites, etc.) has been done, such an analysis can verify the tendency of the released particles to remain embedded or exist in free state. Such tasks are normally accompanied using transmission electron microscopy (TEM). As far as the analysis of various surface phenomena is concerned, it can be done by using atomic force microscope (AFM), scanning electron microscope (SEM), and profilometer. However, these techniques can be roughly divided in two categories: high and ultrahigh resolution. High resolution techniques involve SEM, TEM, and profilometry, whereas AFM is involved in the applications where ultrahigh resolution of a surface is required.

High Resolution. Many wear related phenomena have been explained on the basis of the microscopic observations of the worn surfaces and wear particles. Figure 3(a) shows TEM micrograph of wear debris of a semimetallic polymer matrix composite brake material generated by a dynamometer [12], whereas Figure 3(b) shows the SEM image of ball-milled sample of the same material.

Figures 3(a), 3(b), and 4 directly demonstrate the effect of temperature and stresses during the two processes as the morphology of ball-milled sample differs from wear debris collected in dynamometer. The TEM image (Figure 4) shows the resulting wear particles obtained during [13] the Taber abrasion of a steel panel embedding zinc oxide particles. It is shown that the particles <100 nm remain embedded in the coarse wear particles.

During the grinding of granite, clay ceramic, steel, and aluminum, [10] carried out TEM analysis of the abraded particles. Figure 5 shows the results. In Figure 5(a), a large number of particles >1 μm in diameter with compact non-spherical geometry are shown which were obtained during the grinding of granite. The micrograph of a large number of compact particles >1 μm with some abraded particles of clay ceramic <1 μm is shown in Figure 5(b). However, TEM images of the abraded particles of steel, as depicted by Figure 5(c), were characterized by open chain-like agglomerates of very fine primary particles indicating nucleation followed by growth through coagulation [10]. In the case of aluminum, again large compact and many nanometer sized particles were observed in the TEM image (Figure 5(d)). But from all the observations, [10] concluded that it was not possible to distinguish a source and generation mechanism by morphology alone.

TABLE 1: Beyond the state of the art of particles' aerosol characterization techniques (source: Nanodevice).

Device name	Measured physical metric	Particles size range	Operation principle	Level of development
DEKATI Low-cost total active surface area monitor	Total active surface area	10 nm–3 μ m	Aerosol particle charging in a unipolar diffusion charger; electrical detection of total amount of charged particles using escaping charge technology.	Operational preprototype
TSI NanoGuard	Number concentration, size distribution, and morphology finger print	<20–450 nm	Electrical mobility classified particle charge concentration measured with two detectors with different response characteristics. Signal thresholds trigger method of operation (integral/size distribution scan/sampling with electrostatic precipitator). Thermal precipitator to continuously sample over 8-hour shift.	Working prototypes; full characterization still underway
Naneum Real-time CNT Monitor	Number concentration	All CNT sources	CNT particles in the air are preselected using certain physical/chemical characteristics of CNT. Individual CNT objects are then counted using optical techniques.	Near market
Naneum Personal nanosampler	Mass concentration and size distribution of nanoparticles	2 nm–5 μ m	Up to three cyclones collect larger particles with a final cut-off of 300 nm. Particles with aerodynamic diameters <300 nm are collected on a series of specially designed diffusion stages, with a variety of substrates.	Near market
Stockholm uni. Sampler/preseparator for aerosol fraction deposited in the anterior nasal region	Depending on the metrics of the used monitor	5–400 nm	Diffusive deposition with separation curves optimized with respect to the ICRP model and ISO/FDIS13138:2011.	Preprototype
Stockholm uni. Sampler/preseparator for aerosol fraction deposited in the gas exchange region	Depending on the metrics of the used monitor	20 nm–5 μ m	Aerodynamic and diffusive deposition with separation curves optimized with respect to the ICRP model and ISO/FDIS13138:2011.	Preprototype
Grimm NanoDevice	Particle number and size	10 nm–27 μ m	Electrical and optical principles, currents, and single particle counting (light scattering).	Preprototype
DTU MEMS-based airborne nanoparticles sensor	Mass concentration and chemical composition	5–300 nm	Particle mass: gravimetry; chemical composition: closed information.	Early stage/still in the lab
KIT Catalytic Activity Aerosol Monitor (CAAM)	Catalytic activity concentration	Any with catalytic activity	Particles sampled for a short time on (heated) filter. Reaction gases added to start catalytic reaction. Detection based on IR absorption of the product gas(es). Reactant gas supply from lecture bottle(s) with flow control.	Proof of concept/preprototype
Fraunhofer IPA CNT-detect	Mass concentration	All CNT sources	Magnetic deposition followed by Raman spectroscopy	Preprototype

Nanoparticles emitted from polycarbonate samples containing 3 wt% CNT by abrasion were analyzed by [11] through TEM. Figure 6 shows their observation. They observed the presence of nanometric polymer particles but no free CNTs. Figure 7(a) shows the TEM picture of the nanoparticles emitted from polycarbonate samples (containing 10 wt% Cu)

by abrasion using a brush. Clearly no visible free copper nanoparticles are observed showing that the nanoparticles are still embedded in the polymer matrix. But when the abrasion was done using a P1200 SiC paper, nanoparticles detached from polymer matrix (Figure 7(b)). In the similar fashion, when an epoxy-carbon nanotube nanocomposite was

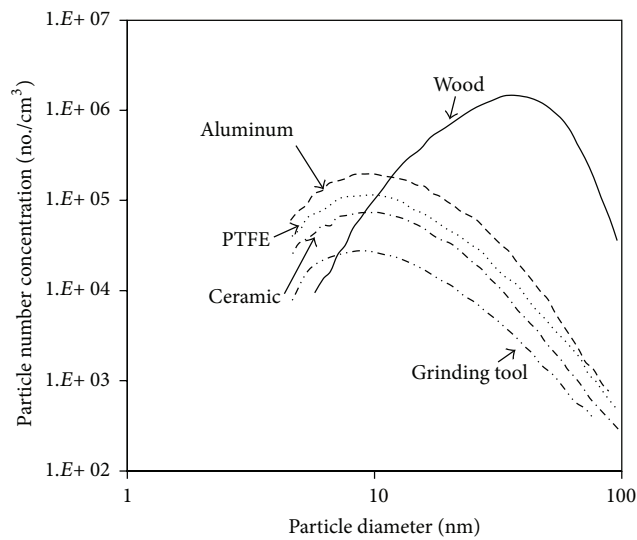


FIGURE 1: Composite of the ultrafine mode experimental results for the Dremel tool and various grinding substrates [10].

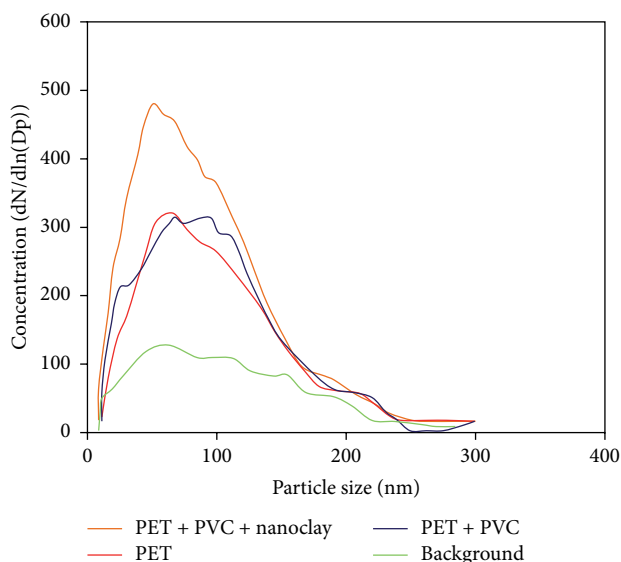


FIGURE 2: Effect of the addition of nanoclay to the PVC coated PET fabrics [11].

abraded using Taber [14], imaging by transmission electron microscopy (TEM) revealed that free-standing individual CNTs get emitted during abrasion. Figure 8 shows the results. Reference [15] carried out sanding of 8 different materials: polyamide (PA) with and without SiO_2 nanoparticles, polyoxymethylene (POM) with and without carbon nanotubes (CNTs), hardened cement paste (CEM) with and without CNTs, and the same paste but with and without calcium silicate hydrate (CSH).

Figure 9 shows the morphology of the emitted particles. They observed that the harder materials, that is, cement, irrespective of the presence of nanofillers, tend to generate significantly lower masses of powder, but in the form of smaller particles, in comparison to the softer materials, that

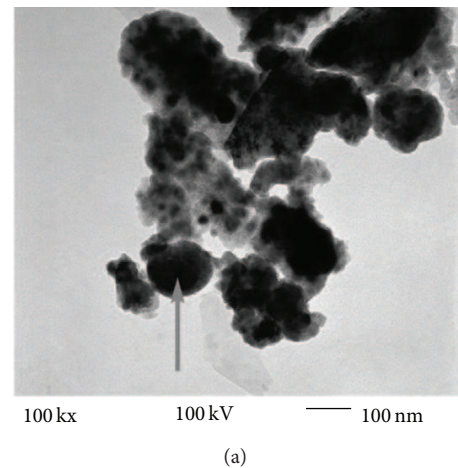
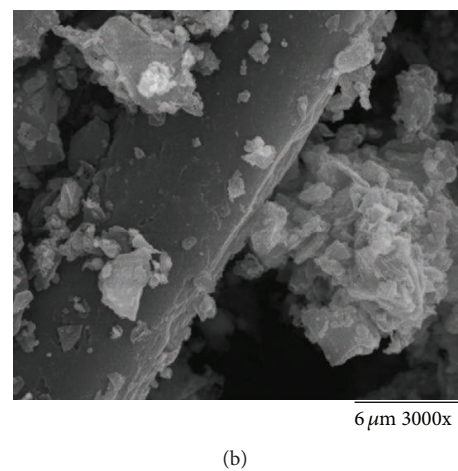


FIGURE 3: (a) TEM micrograph of wear debris [12]; (b) SEM image of fiber found in milled pad sample [12].

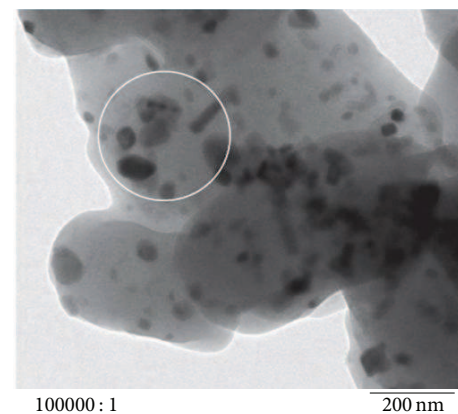


FIGURE 4: TEM image of wear from the steel panel with embedded zinc oxide particles [13].

is, thermoplastics. The size distribution was found to be dominated by a large fraction between typically 10 and 80 μm . For a detection threshold of 100 ppm, they were not able to detect any free nanofiller.

Reference [16] did the abrasion of filled and unfilled carbon fabric composites against an AISI-1045 steel pin using

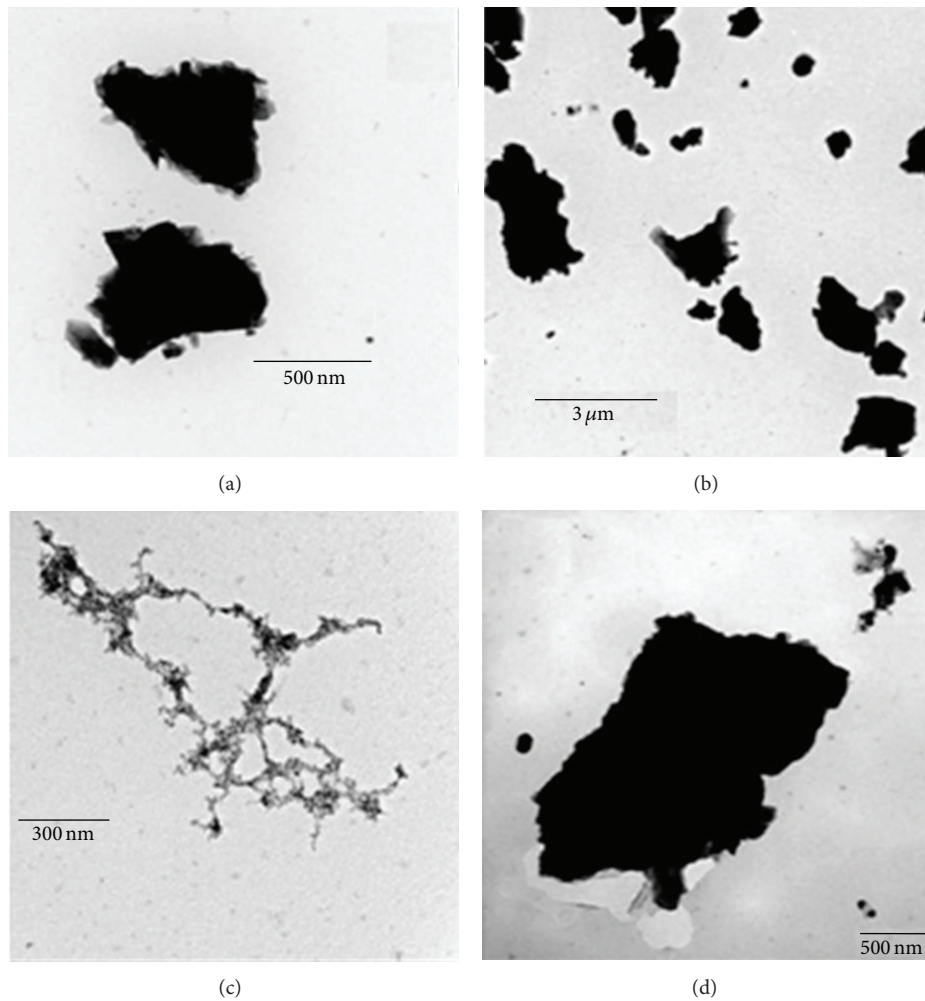


FIGURE 5: TEM micrographs of the various grinding substrates [10].

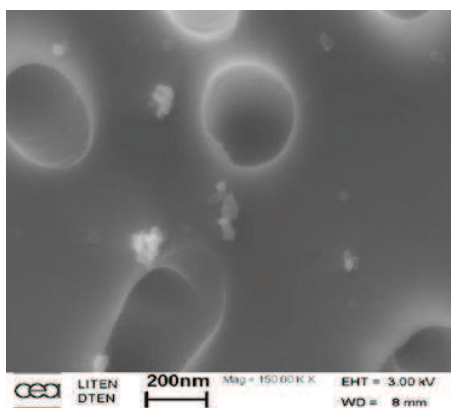


FIGURE 6: SEM observation of detected particles on filter out on the ELPI channel abraded using a steel brush [11].

a pin-on-disc arrangement. From Figure 10, showing SEM of the worn carbon fabric composites, it can be observed that most of the carbon fibers are pulled out from the fabric matrix on the worn surface of the unfilled carbon fabric

composite (see Figure 10(a)), which indicates that the pure carbon fabric composite undertook a large contact stress and experienced severe peeling off as it slid against the steel at room temperature. Contrary to the above, the worn surface of the carbon fabric composite filled with 25% Polyfluor Wax is smooth and the pulling-out and exposure of the carbon fibers are nearly invisible (see Figure 10(b)).

Moreover, the worn surface of the carbon fabric composite filled with 8% nano-ZnO or 5% nano-SiC is relatively smooth but still shows signs of carbon fiber pull-out (see Figures 10(c) and 10(d)), which agree well with the friction and wear behaviors of the composites filled with nano-ZnO and nano-SiC. Reference [17] recorded the abrasion behavior of the same steel under two different abrasion conditions: pin-on-disc and paddle wear test. For consistency, they checked the behavior difference for 2 other grades of steel. Figures 11 and 12 show the difference between the surface characteristics obtained in two different wear conditions. As can be seen, the contact conditions active in the paddle wear test, that is, mainly impact abrasion and some sliding abrasion, generate heavily deformed surfaces with a relatively high amount of embedded fragments. In contrast, the contact conditions in

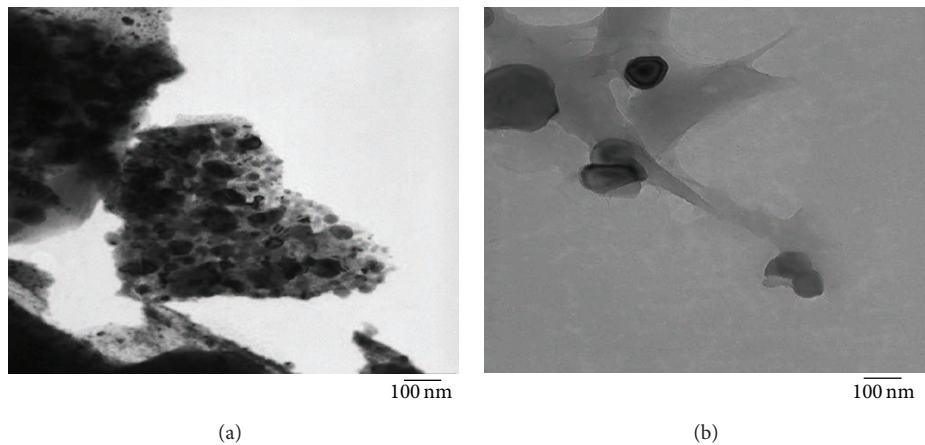


FIGURE 7: (a) TEM observation of detected particles abraded using a steel brush [11]; (b) TEM observation of detected particles abraded using a P1200 SiC paper [11].

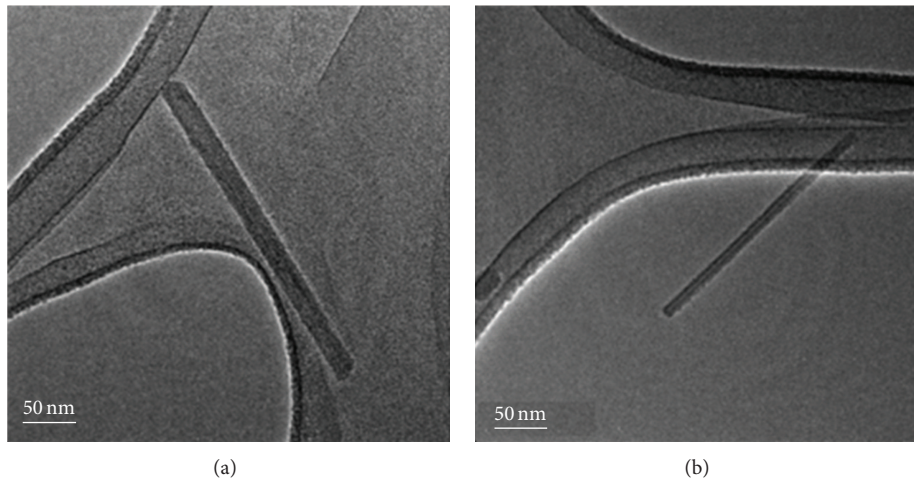


FIGURE 8: TEM images of free-standing individual CNTs [14].

the pin-on-disc test, that is, two-body abrasion, generate relatively well-defined worn surfaces without any embedded fragments. Characterization of the worn surfaces using 3D surface profilometry illuminates the pronounced difference in surface morphology, that is, the degree of surface plastic deformation, between specimens exposed to the two types of wear tests; see Figure 13.

Ultrahigh Resolution. This type of resolution is mainly required for analysis and control of the contact interactions between micro, or nanosized particles and nanomaterials surface topography. An understanding of these interactions is critical for any application that relies upon nanomaterials manipulation. AFM is used as a vital tool in understanding the fundamental mechanisms of particulate processes. Its use is further accompanied by a possible means to study the wear phenomena at atomic level. Reference [50] provides a greater insight into the influence of particle micro- and nanoroughness on adhesion by using AFM technique to determine

an effective asperity radius of curvature for the contacting particle in the contact zone topography of glass and UO_3 particles in contact with flat mica substrates. Reference [51] reviews briefly the measurements and interpretation of adhesion forces between microscopic probes and substrates having micro- and nanoscaled roughness characteristics. The study was concentrated on both rigid and deformable materials, with the probes larger than the size of roughness features of interacting surfaces. They concluded that controlling the deformation reduces and even eliminates the effects of nanoroughness on the probe-substrate contact area, promoting conditions described by the contact mechanics models (to be discussed in next section) for the sphere-smooth substrate system. AFM finds another application in the exploration of the range of interaction forces [52] which can be utilized to predict, optimize, and design a variety of industrially relevant processes such as chemical mechanical polishing (CMP), powder flow and handling, and nanodispersions. Towards the resolution of the problem of

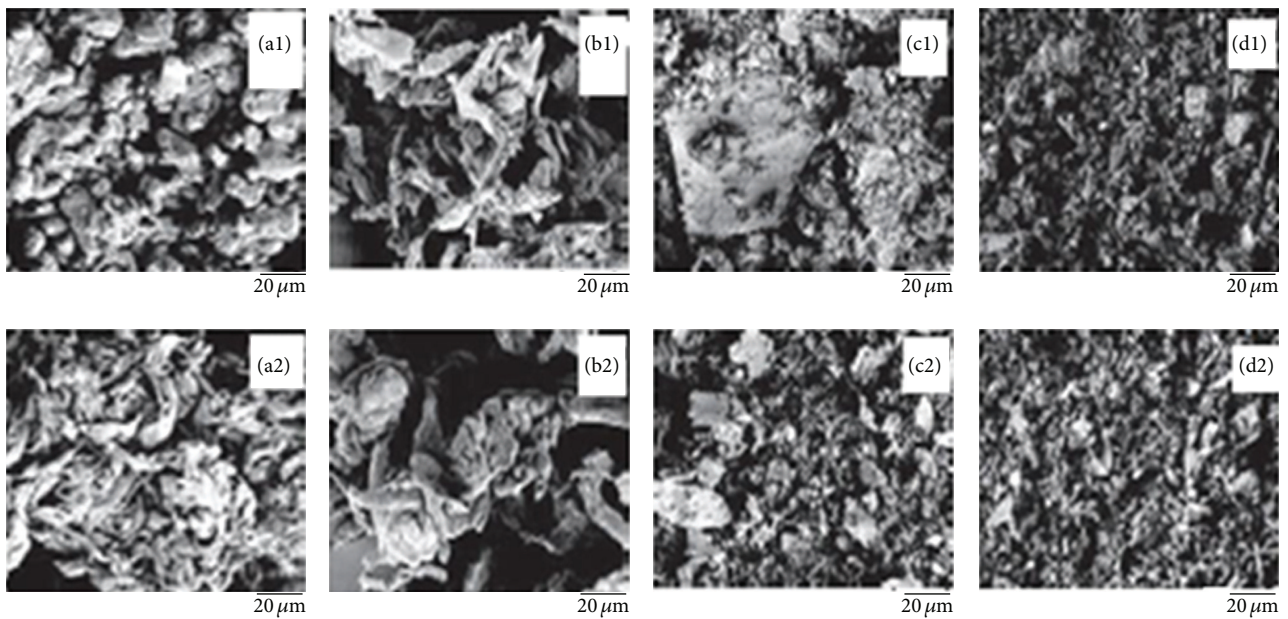


FIGURE 9: SEM images of powders generated by sanding nanocomposites and their reference materials [15]. (a) PA with (a1) and without (a2) SiO_2 , (b) POM with (b1) and without (b2) CNTs, (c) CEM with (c1) and without (c2) CNTs and (d) CEM with (d1) and without (d2) CSH.

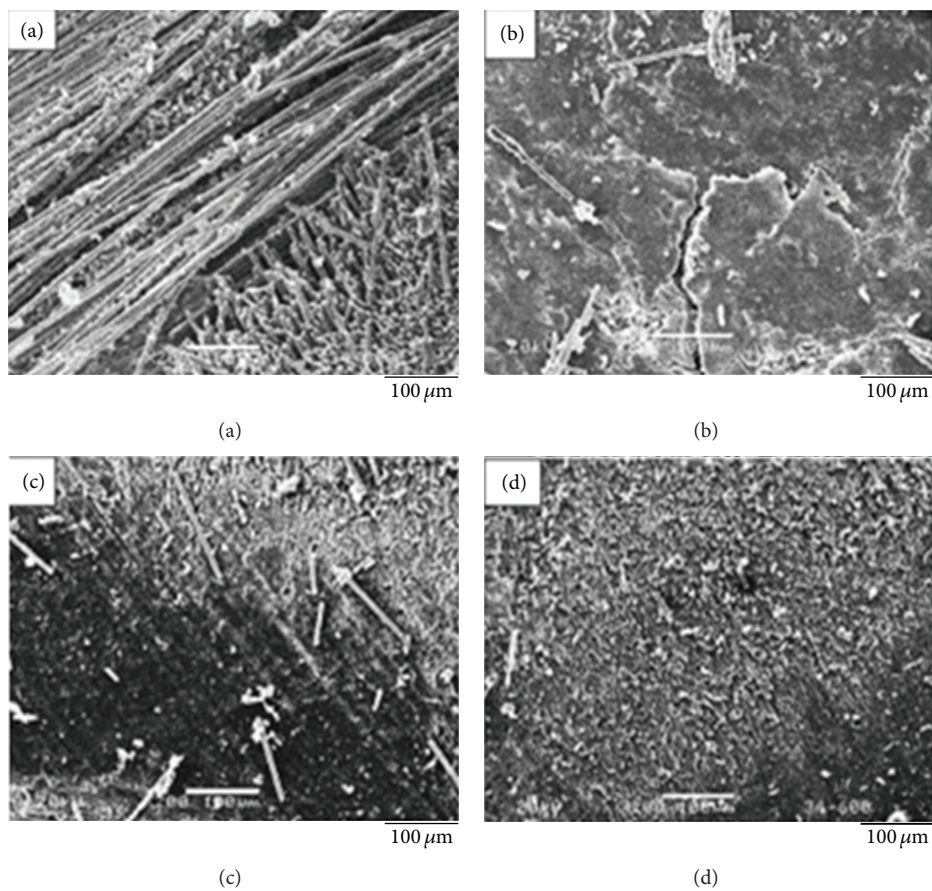


FIGURE 10: SEM morphologies of the worn surfaces of carbon fabric composites reinforced with different fillers at 274.4 N and room temperature: (a) pure CFC; (b) CFC + 25% PFW; (c) CFC + 8% nano-ZnO; (d) CFC + 5% nano-SiC [16].

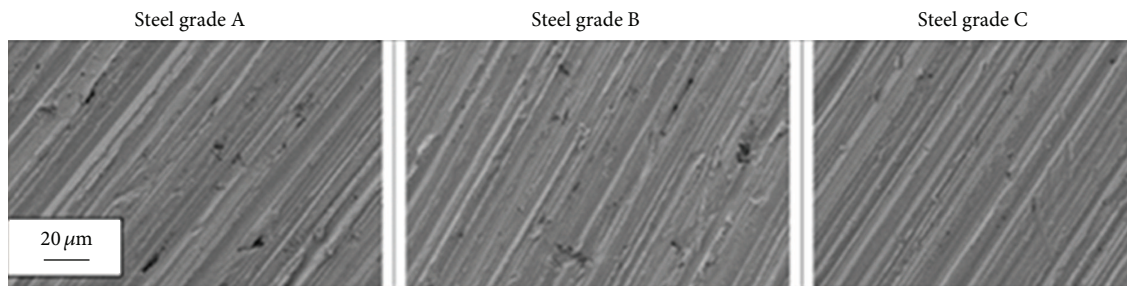


FIGURE 11: Surface characteristics of worn surfaces of the steel grades investigated when exposed to the pin-on-disc test as observed in the SEM [17].

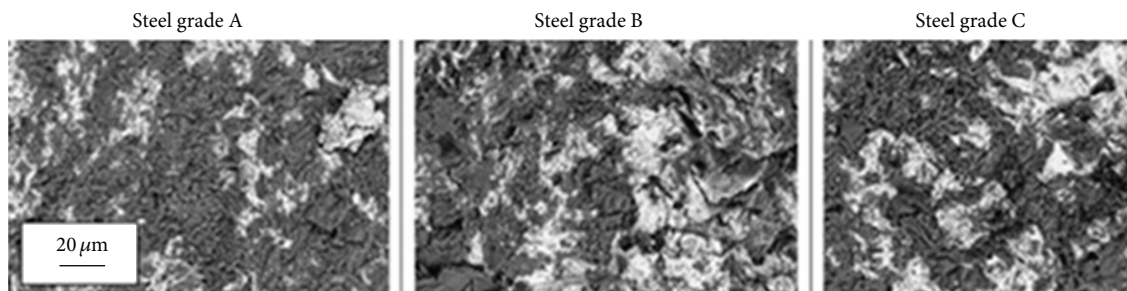


FIGURE 12: Surface characteristics of worn surfaces of the steel grades investigated when exposed to the paddle wear test as observed in the SEM [17].

powder flow by reducing the interparticle adhesion force, [53] indicated that their method of quantifying the interparticle adhesion force using AFM may be used to predict flow behavior of original (cohesive) and surface modified (previously cohesive) powders utilizing very small samples and that the surface modification can drastically improve the powder flow for industrially relevant materials. A similar intergranular adhesion study was carried out by [54] which reviews progress in micro/nanoparticle manipulation and particle-substrate adhesion studies. It found AFM to be the most commonly used tool for particle manipulation studies.

A new approach using AFM was proposed by [55] to carry out 3D numerical surface characterization of wear debris generated from artificial joints. The method developed from the study was found to be feasible to quantify the surface characterization of nano- and micro-sized wear particles. Emphasizing on the dependency of the wear particles aerosol generation on the material properties like viscoelastic and fracture properties of one of the widely used polymeric materials, epoxy resin, [56] concluded that such material properties can be tailored by changing the network or crosslink structure by blending monomers with different molecular weights which were characterized using AFM. On a similar type of substrate, [57] performed some nanoscratch tests and studied surface morphology using AFM tip. Reference [58] used AFM tips to simulate a sharp single asperity travelling over a stainless steel surface and demonstrated that nanowear experiments, at controlled contact pressures and scanning speeds, can be performed in almost any type of material. The same AFM enabled them to observe and characterize the nano/micro worn regions with a high lateral resolution.

Although AFM can image surfaces with a nanometer spatial resolution, the finite size of standard tips means that pores, pits, or grooves with dimensions similar to or smaller than the tip apex will not be accurately imaged. Furthermore, standard tips are made of silicon or silicon nitride which are prone to wear when subjected to stress. In this effect, [59] performed tests to compare the imaging performance of ultrasharp Si AFM tips, CNT AFM tips prepared by a Langmuir-Blodgett (LB) technique, and CNT AFM tips prepared by a chemical vapor deposition (CVD) technique. In general, ultrasharp Si tips allowed for a remarkably good resolution of the height variations in niobium film with a nanoscale polycrystalline structure. Their height resolution was found to be excellent although their lateral resolution was not as good as the one of CNT AFM tips.

3. Theoretical Modeling

Modeling of wear processes allows identifying the most important factors influencing wear and hence aerosol generation. Due to this reason, more than a century has been spent for searching such models which are both general and based on fundamental aspects. However, this search is still elusive. Reference [60] established the first wear model in which the wear volume rate is shown to be proportional to the normal load. Holm considered the plastic deformation as the predominant mechanism for the material removal. In the classical abrasive wear model proposed by Archard, the wear volume is predicted to be a function of sliding distance, the applied normal load, and the material hardness. In 1962, [61] presented a simple model for the abrasion of steel sliding

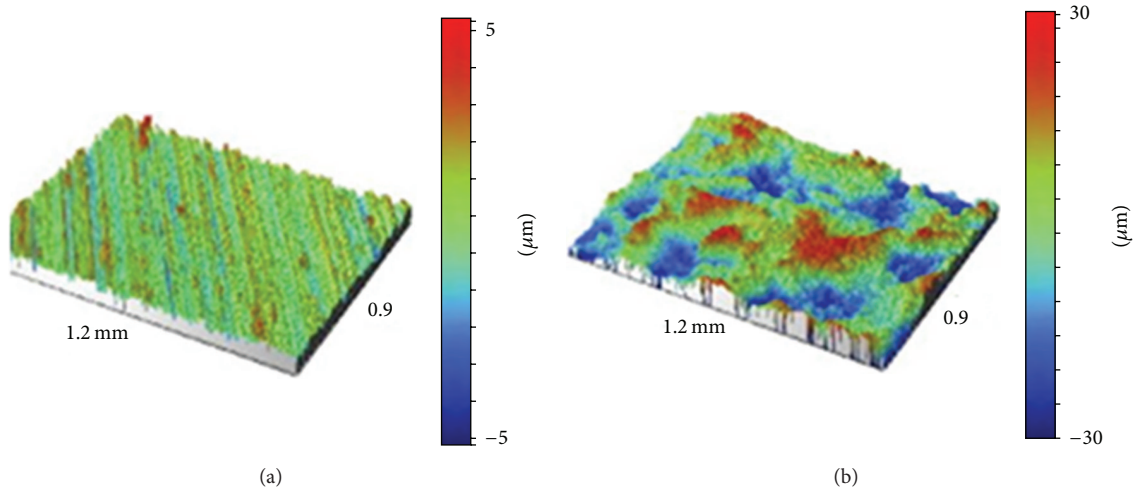


FIGURE 13: 3D surface profiles of worn specimens of steel grade A exposed to the pin-on-disc test (a) and the paddle wear test (b) [17].

against silicon carbide paper. The model takes into account the shape of the contacting abrasive particles, their attitude in the abrasive paper, and their deterioration with use. Other more detailed models have also been developed to predict the abrasive rates of materials under specific conditions. Reference [62] stated hardness to be the most important property that determines the wear rate. This model is simple and provides a qualitative theoretical basis. But later extensive studies have shown that the other properties can significantly affect the abrasive wear and the predicted wear coefficient is at least an order of magnitude larger than experimentally observed values. Reference [63] proposed a model for wear of brittle solids under fixed abrasive conditions. Reference [64] presented a model for two-body abrasive wear based on localization of plastic deformation. This model assumes that the localization of deformation in the near-surface regions underneath the abrasive grains is responsible for the wear generation. From this onwards, it started being understood that the correct wear behavior can be identified by inculcating the factors accounting for plasticity and governing yield criteria. Reference [20] has used the theoretical analysis of the steady state of two sliding asperities to investigate the mechanics involved in the sliding contact of two rough surfaces (one hard and one soft). Their analysis was restricted to the case when the roughness on the harder surface is regular, that is, all asperities have the same height and curvature, and it is only the soft surface that is randomly rough, that is, asperities with a Gaussian height distribution and constant curvature.

Some models [65] also incorporate various thermophysical and slip line field analysis methods. Most of the existing models, however, mainly deal with single particle contact conditions. Reference [66] tried to justify the wear by studying the frictional force evolution with the combined sliding between two bodies. He explained the transition between the micro and macro/gross displacement/slip experimentally and showed that it can proceed in a number of ways. The total frictional force, $F = F_{\text{spring}} + F_{\text{slip}} \cdot F_{\text{spring}}$, is the frictional load from the active asperities which have not reached

their limiting elastic limit and F_{slip} is the contribution from asperities which have reached their elastic limit:

$$F = \frac{8}{15} \mu C A_0 E^* R^{1/2} \left[\lambda^{5/2} - \left(\lambda_n - \frac{4G^* \delta}{\mu E^*} \right)^{5/2} \right], \quad (1)$$

where μ is the coefficient of friction, C is the constant relating the number of contacts per unit area and the approach of the surfaces, A_0 is the apparent area of contact, E^* is the composite modulus of elasticity of two bodies having their respective elastic moduli as E_1 and E_2 :

$$\frac{1}{E^*} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2}, \quad (2)$$

R is the spherical asperity radius, λ_n is the normal approach, δ is the tangential displacement of the asperity, and G^* is the composite shear modulus of two bodies having their respective moduli as G_1 and G_2 :

$$\frac{1}{G^*} = \frac{2 - \nu_1}{G_1} + \frac{2 - \nu_2}{G_2}. \quad (3)$$

Reference [67] presented a general wear model for wear rate and specific wear energy of materials in two-body abrasive wear (one hard and one soft) under multiple contact conditions by considering wear mode transitions and material removal fraction. Using the proposed model, the authors showed typical variations of wear rate as a function of grit size of the abramer, thereby explaining the grit size effect:

$$K = \frac{V}{PS} = \frac{N A_a}{P} \int_{h_m}^{h_z} f(z) A_i \beta dz, \quad (4)$$

where N is the number of abrasive particles on unit area of the hard material, A_a is the apparent area of contact, P is the apparent contact pressure, h_z is the maximum height of an asperity, h_m is the mean height, $f(z)$ is the asperity height distribution, A_i is the cross section area of a groove

produced in the soft material by abrasion of an individual abrasive particle, and β is the fraction of material removed from the groove produced. For the first time, [68] introduced numerical methods, in particular, Monte Carlo, to model a two-body abrasion process. The model is also compared with experimental values and the results were found to be in agreement with each other. In the model, the grit was considered to be in conical shape with the geometry parameters—height, radius of the tip, position distribution, and conical angle—as the input variables. Reference [69] provided an energy description of the wear mechanisms in hard TiN and TiC coatings during oscillating sliding contacts. Reference [70] pointed out that the abrasive wear rates of materials may be very simply related to their mechanical properties, provided wear takes place under very simple conditions. However, wear rates in many practical situations can be controlled by effects which either relate to mechanical properties in more subtle ways or which are controlled by quite different parameters. Mechanics models of the abrasive process provide a means of linking these different effects together to understand better the effects, which may determine wear under particular conditions. They can also help to design tests to measure the properties of a material under conditions similar to those pertaining in abrasion. With the argument that the abrasion process varies substantially from one material pair to another during a single test, [71] put forward a wear law for Boron Carbide (B_4C) coatings when slid against AISI 52100 steel. The wear law suggests that the total abrasion rate is the function of the volume of the steel removed and total sliding distance. Abrasion experiments were carried out under various contact conditions, dry or wet, and corresponding values of the variables were calculated for every condition. Recently [72] understood the value of theoretical modeling of wear for designing and optimizing tribological systems, particularly during unlubricated conditions. They presented a generic, asperity level, theoretical model for predicting wear evolution in a plain contact. They have justified the material removal by saying that, when the energy accumulation in an asperity, owing to repeated elastic-plastic deformation, exceeds a certain threshold, the asperity breaks off. The simulation results show, both for unidirectional and bidirectional sliding, a qualitative agreement with experimental observations. Apart from the running-in process, a linear trend was observed between the wear volume and the energy dissipation in the contact. References [73, 74] modeled fretting behavior of nominally flat rough surfaces. Individual asperity-scale contact forces have been formulated and added statistically to each other to obtain the fretting response of a flat rough contact.

4. Conclusion and Discussions

In the present paper, different aspects towards the study of the wear particles have been presented after a thorough investigation and review of the contemporary studies. The primary focus of this paper is to develop a state of art of the interdisciplinary studies conceived towards the aerosolization of wear particles. It has been found that there has been

no significant progress towards the measure of the wear particles aerosols. Despite a widespread use of various wear test methods and various steps of the nanoparticle's life cycle assessment, the measure of in-process generation of wear particles aerosols is still an interdisciplinary challenge, and finds only impact on few norms. The fundamental studies which were conceived in this direction have dealt with this aspect experimentally with a limited scope. There has already been a wide scale development of the instrumentation for particles aerosols characterization. However, it mainly suffers from its semiquantitative approach (due to the exclusion of the stray particles generated during wear process) and inability of the separation of the particles under study from background noise on an industrial scale. Hence, various reliable, robust, novel, portable, and easy-to-use instruments for characterizing wear particles are required for the next generation technology which is able to couple particle release characterization to wear scenarios in a standardized way.

Apart from the experimental scenario, the theoretical understanding of various underlying physical phenomena and identification of their key parameters giving rise to the aerosolization of the wear particles need much attention. Both theoretical and experimental approaches are complementary to each other to foresee beyond the state of the art so as to identify and understand the in-process occurring physical phenomena.

From the present study we can infer that in spite of various limitations, the past studies provide sufficient background and platform to continue the intended study in the direction suggested. It is on the basis of the investigation of these studies only that one can enlist some of the possible major factors affecting the quantity, morphology, size, nature, and mechanism of generation of the wear particles aerosols.

(1) *Surface Conditions.* These conditions mainly include the roughness and porosity of the surface. However, if there is any physical treatment like application of a coating through pulverization, chemical treatment like etching, and mechanical treatment like machining, generation of wear particles aerosols can be equally affected. The properties like isotropicity, anisotropicity, and photogenicity of a surface also play an important role in this aspect.

(2) *Stress Conditions.* The value of the load acting on the surface and its nature, that is, static or dynamic, is also important towards the particles aerosols generation as it is the deciding factor for the occurrence of an elastic or plastic or elastoplastic deformation of the surface during abrasion which later gives rise to fracture nucleation.

(3) *Temperature Dissipation.* The temperature dissipation is very decisive in the ductile surfaces like metals. It is the dissipation or accumulation of the heat that results in the progressive adhesion of the wear particles which may or may not inhibit the further wear. Also it renders an indecisive deterioration of the surface.

(4) *Contact Condition.* This factor cannot be considered as totally independent from other conditions but it would be

much simpler to consider it separately while formulating the wear particles aerosol. These conditions include the interference of the two mating surfaces produced when brought in contact. With specific surface and stress conditions, there may be a development of stress concentration which can enhance the aerosol generation. The adhesion of the surfaces to each other also depends on the contact conditions.

(5) *Nature of the Material.* The material properties like hardness, brittleness, ductility, and so forth seem to affect the aerosol generation. Incrystalline solid, molecular structure and forces contribute towards the inbuilt surface forces or tension which further decides the stability of surface.

In order to foresee beyond the state of the art, the eradication of some common limitations in all the studies done to this date is required. One of the major problems in the wear models presented up to date has been the lack of the representation of real surface geometric complexities due to the mathematical, physical, and experimental intricacies. It needs to be eliminated and should be supported by numerical methods in order to be more reliable and efficient. Also, the future works should inculcate various phenomenological, micromechanical, and microscale interactions between the mating surfaces. Ultrahigh resolution microscopy finds its use here. The wear tests should be coupled to real life industrial case studies which could contribute to future standardization activities. A new generation of sampling methods for use in industry could aid such a coupling.

With this, one should also not forget that the science behind the wear generation in the engineering materials is always evolving with the evolution of the materials with time. In the present study, it has been found that an important milestone in the studies of the wear generation, owing to surface microscopic studies, has been the transition of the studies from the macroscopic interactions to microscopic interactions of the surfaces. Therefore, there arises a need to have another milestone of the transition from microscopic to nanoscopic interactions. This will allow having a sufficient theoretical basis to study the nanometric wear particles aerosols. This transition becomes more pertinent with present overwhelming use of manufactured nanomaterials (MNM) in the commercial products due to which more and more humans are susceptible towards the exposure of the nanoparticles aerosol which may pose big health problems.

Therefore, such an approach may prove to be a major contribution in the sustainable and durable development of the technology so as to have *nanosafety by design* rules for nanoproducts.

5. Annexure

This section describes the solicitation methods used in the studies mentioned in the paper along with the references where they are employed.

5.1. Taber Abrasion Tester. As employed by [13, 30, 31], Taber abraser is a well-known abrading method. Its use is widespread and is described in many national and international standards (e.g., DIN 53754:1977, DIN 68861-2:1981,

ISO 5470-1:1999, ASTM C 1353-07, and ASTM D 4060-95:2007). In this system, a horizontal arm is incorporated that reciprocates in a linear motion. Attached to the end of the arm is a precision bearing spline shaft that creates a “free-floating” test system and permits vertical movement. The test attachments are affixed to the bottom of the spline shaft and a weight support is mounted to the top. As the horizontal arm strokes back and forth, the test system rises or lowers vertically as the test attachment follows the contours of the specimen. Reference [27] generated sanding dust using a commercial hand-held orbital sander with an internal fan for dust removal. A sand paper with fine grit size was employed to enhance the chances of fine particles generation.

5.2. Ball Milling. The process of ball milling is a type of grinding in which a cylindrical device is used in grinding or mixing materials. Ball mills rotate around a horizontal axis, partially filled with the material to be ground plus the grinding medium. Different materials are used as media, including ceramic balls, flint pebbles, and stainless steel balls. An internal cascading effect reduces the material to a fine powder with particle size range in submicrons. Reference [12] ball milled semimetallic polymer matrix composite brake linings using a laboratory vibrating ball mill VM4 with tungsten carbide beads. The brake pads were removed from the backing plates, cut into segments of approximately 1 cm^3 , and repeatedly ball milled for 10 min and sieved through a $200\text{ }\mu\text{m}$ sieve until sample particles with major fractions below $200\text{ }\mu\text{m}$ were obtained.

5.3. Dynamometer. Reference [12] used a full scale brake dynamometer in an environmental chamber with wind tunnel simulating airflow. The dynamometer was fed with two semimetallic polymer matrix composite brake linings, each weighing 113 g, in eight tests. Each lining set was run twice consecutively, the first run using a resurfaced brake rotor and the second using the same rotor from the first run without any changes. Wear debris collected from the dynamometer was sieved using USA Standard Testing Sieve.

5.4. Ultraviolet Photodegradation and Chemical Treatment. These methods of wear treatment, through degradation, are applicable for the polymeric compounds or the organic coatings in order to evaluate their durability as well as mechanical and thermal properties. Knowledge of aging behavior and mechanism of these materials is of great help for antiaging research. References [75, 76] studied the photodegradation mechanism and after products of polypropylene (PP) nanocomposites. Similarly, [77] also studied these nanocomposites, namely, PP/CaCO₃ and PP/SiO₂, outdoor for 88 days against unfilled PP. They found that the PP nanocomposites are more susceptible to photodegradation than the unfilled ones and, therefore, have higher tendency for wear. Also, the oxidation rate increases with the filler amount.

Chemical treatment on the surface layer is mainly done by the commercial mirror manufacturers. The layer is composed of the layers or films of copper or silver. Within standard testing methods, the copper chloride modified acetic acid

salt spray test is employed (CASS test, NF ISO 9227 12/1991). During this test, the surface layer on the mirrors shows macroscopic degradation of the metallic layers from the edges and more randomly at the centre of the samples. Reference [78] adopted this methodology and carried out infrared spectroscopy for their study.

5.5. Emission Chamber. Although this technique is not directly responsible for the wear generation, hence the aerosol generation, but it acts as an interconnection between the aerosols generation mechanism and their measurement mechanism. It is a sampling hood which almost completely encapsulates the sample suction zone behind the aerosol particles generation site. With the help of the emission chamber, particle loss in the air flow of the laminar low box can be avoided. This technique has been widely adopted by [10, 11, 13, 27, 48] for ensuring very low or zero background particles presence.

5.6. Grinders and Sanders. Grinding and sanding are most common operations in the workshops. In order to assess the safety associated with these processes, there have been many attempts. Reference [47] did an investigation on the production of dust by hand sanders. Reference [10] worked on the aerosols generated by using a *Multipro Dremel* Grinder, model 395, with a variable speed tool having rotational speed from 5000 to 30 000 rpm. A cylindrical grinding wheel, composed of sintered aluminum oxide, was used for the experiments. Reference [27] performed sanding of nanoparticles containing paints using a commercial hand-held orbital sander (*Metabo* Model FSR 200 Intec) with an internal fan for dust removal. Grit size 240 sanding paper was used for sanding.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] P. Kulkarni, P. A. Baron, and K. Willeke, *Aerosol Measurement: Principle, Techniques and Applications*, John Wiley and Sons, Hoboken, NJ, USA, 3rd edition, 2011.
- [2] G. Oberdörster, E. Oberdörster, and J. Oberdörster, "Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles," *Environmental Health Perspectives*, vol. 113, pp. 823–839, 2005.
- [3] P. Houdy, M. Lahmani, and F. Marano, *Nanoethics and Nanotoxicology*, Springer, Heidelberg, Germany, 1st edition, 2011.
- [4] C. Bekker, D. H. Brouwer, E. Tielemans, and A. Pronk, "Industrial production and professional application of manufactured nanomaterials-enabled end products in Dutch industries, potential for exposure," *The Annals of Occupational Hygiene*, vol. 57, no. 3, pp. 314–327, 2012.
- [5] S. Kaluza, J. K. Balderhaar, B. Orthen et al., "Workplace exposure to nanoparticles," 2010.
- [6] C. Buzea, I. I. P. Blandino, and K. Robbie, "Nanomaterials and nanoparticles: sources and toxicity," *Biointerphases*, vol. 2, no. 4, pp. MR17–MR172, 2007.
- [7] Scientific Committee on Emerging and Newly Identified Health Risks (SCENIHR), "The appropriateness of existing methodologies to assess the potential risks associated with engineered and adventitious products of nanotechnologies," Health and Consumer Protection Directorate-General, European Commission, 2006.
- [8] C. Ostiguy, B. Roberge, L. Ménard, and C. A. Endo, "Best Practices Guide to Synthetic Nanoparticle Risk Management, L'Institut de recherche Robert-Sauvé en santé et en sécurité du travail (IRSST)," Report R-599, 2009.
- [9] National Institute for Occupational Safety and Health (NIOSH), "Centers for Disease Control and Prevention (CDC), Approaches to Safe Nanotechnology," Publication 2009-125, 2009.
- [10] A. T. Zimmer and A. D. Maynard, "Investigation of the aerosols produced by a high-speed, hand-held grinder using various substrates," *Annals of Occupational Hygiene*, vol. 46, no. 8, pp. 663–672, 2002.
- [11] A. Guiot, L. Golanski, and F. Tardif, "Measurement of nanoparticle removal by abrasion," *Journal of Physics*, vol. 170, Article ID 012014, 2009.
- [12] J. Kukutschová, V. Roubíček, K. Malachová et al., "Wear mechanism in automotive brake materials, wear debris and its potential environmental impact," *Wear*, vol. 267, no. 5–8, pp. 807–817, 2009.
- [13] M. Vorbau, L. Hillemann, and M. Stintz, "Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings," *Journal of Aerosol Science*, vol. 40, no. 3, pp. 209–217, 2009.
- [14] L. Schlagenhauf, B. T. T. Chu, J. Buha, F. Nüesch, and J. Wang, "Release of carbon nanotubes from an epoxy-based nanocomposite during an Abrasion process," *Environmental Science and Technology*, vol. 46, pp. 7366–7372, 2012.
- [15] W. Wohlleben, S. Brill, M. W. Meier et al., "On the lifecycle of nanocomposites: comparing released fragments and their in-vivo hazards from three release mechanisms and four nanocomposites," *Small*, vol. 7, no. 16, pp. 2384–2395, 2011.
- [16] Z.-Z. Zhang, F.-H. Su, K. Wang, W. Jiang, X.-H. Men, and W.-M. Liu, "Study on the friction and wear properties of carbon fabric composites reinforced with micro- and nano-particles," *Materials Science and Engineering A*, vol. 404, no. 1-2, pp. 251–258, 2005.
- [17] J. Rendón and M. Olsson, "Abrasive wear resistance of some commercial abrasion resistant steels evaluated by laboratory test methods," *Wear*, vol. 267, no. 11, pp. 2055–2061, 2009.
- [18] F. P. Bowden and D. Tabor, *The Friction and Lubrication of Solids*, Clarendon Press, Oxford, UK, 1954.
- [19] A. P. Green, "Friction between unlubricated metals: a theoretical analysis of the junction model," *Proceedings of the Royal Society A*, vol. 228, pp. 191–204, 1955.
- [20] A. Kapoor, J. A. Williams, and K. L. Johnson, "The steady state sliding of rough surfaces," *Wear*, vol. 175, no. 1-2, pp. 81–92, 1994.

- [21] U. Olofsson and L. Hagman, "Model for micro-slip between flat surfaces based on deformation of ellipsoidal elastic bodies," *Tribology International*, vol. 30, no. 8, pp. 599–603, 1997.
- [22] P. J. Blau, *Friction, Lubrication, and Wear Technology Vol. 18*, ASM Handbook, 1992.
- [23] O. Le Bihan, N. Shandilya, L. Gheerardyn, O. Guillon, E. Dore, and M. Morgeneyer, "Investigation of the release of particles from a nanocoated product," *Advances in Nanoparticles*, vol. 2, pp. 39–44, 2013.
- [24] K. Hokkirigawa and K. Kato, "An experimental and theoretical investigation of ploughing, cutting and wedge formation during abrasive wear," *Tribology International*, vol. 21, no. 1, pp. 51–57, 1988.
- [25] M. A. McCawley, M. S. Kent, and M. T. Berakis, "Ultra-fine beryllium number concentration as a possible metric for chronic beryllium disease risk," *Applied Occupational and Environmental Hygiene*, vol. 16, no. 5, pp. 631–638, 2001.
- [26] K. T. Choe, M. Trunov, S. A. Grinshpun et al., "Particle settling after lead-based paint abatement work and clearance waiting period," *The American Industrial Hygiene Association Journal*, vol. 61, no. 6, pp. 798–807, 2000.
- [27] I. K. Koponen, K. A. Jensen, and T. Schneider, "Sanding dust from nanoparticle-containing paints: physical characterisation," *Journal of Physics*, vol. 151, Article ID 012048, 2009.
- [28] B. D. Garg, S. H. Cadle, P. A. Mulawa, P. J. Groblicki, C. Laroo, and G. A. Parr, "Brake wear particulate matter emissions," *Environmental Science and Technology*, vol. 34, no. 21, pp. 4463–4469, 2000.
- [29] P. G. Sanders, N. Xu, T. M. Dalka, and M. M. Maricq, "Airborne brake wear debris: size distributions, composition, and a comparison of dynamometer and vehicle tests," *Environmental Science and Technology*, vol. 37, no. 18, pp. 4060–4069, 2003.
- [30] H.-J. Gläsel, F. Bauer, H. Ernst et al., "Preparation of scratch and abrasion resistant polymeric nanocomposites by monomer grafting onto nanoparticles," *Macromolecular Chemistry and Physics*, vol. 201, no. 18, pp. 2765–2770, 2000.
- [31] O. Knotek, E. Lugscheider, F. Löffler, G. Krämer, and H. Zimmermann, "Abrasive wear resistance and cutting performance of complex PVD coatings," *Surface and Coatings Technology*, vol. 68–69, pp. 489–493, 1994.
- [32] L. Reijnders, "The release of TiO₂ and SiO₂ nanoparticles from nanocomposites," *Polymer Degradation and Stability*, vol. 94, no. 5, pp. 873–876, 2009.
- [33] J. K. Pandey, K. Raghunatha Reddy, A. Pratheep Kumar, and R. P. Singh, "An overview on the degradability of polymer nanocomposites," *Polymer Degradation and Stability*, vol. 88, no. 2, pp. 234–250, 2005.
- [34] X. D. Chen, Z. Wang, Z. F. Liao, Y. L. Mai, and M. Q. Zhang, "Roles of anatase and rutile TiO₂ nanoparticles in photooxidation of polyurethane," *Polymer Testing*, vol. 26, no. 2, pp. 202–208, 2007.
- [35] R. Kaegi, A. Ulrich, B. Sinnet et al., "Synthetic TiO₂ nanoparticle emission from exterior facades into the aquatic environment," *Environmental Pollution*, vol. 156, no. 2, pp. 233–239, 2008.
- [36] W. Wohlleben, M. W. Meier, S. Vogel et al., "Elastic CNT-polyurethane nanocomposite: synthesis, performance and assessment of fragments released during use," *Nanoscale*, vol. 5, pp. 369–380, 2013.
- [37] L.-Y. Hsu and H.-M. Chein, "Evaluation of nanoparticle emission for TiO₂ nanopowder coating materials," *Journal of Nanoparticle Research*, vol. 9, no. 1, pp. 157–163, 2007.
- [38] S. Sachse, F. Silva, H. Zhu, A. Irfan, A. Leszczynska, and K. Pielichowski, "The effect of nanoclay on dust generation during drilling process of polyamide 6 nanocomposites," *Nanomaterials*, vol. 2012, Article ID 189386, 8 pages, 2012.
- [39] D. Gohler, M. Stintz, L. Hillemann, and M. Vorbau, "Characterization of Nanoparticle release from surface coatings by the simulation of a sanding process," *Annals of Occupational Hygiene*, vol. 54, pp. 615–624, 2010.
- [40] M. Morgeneyer, O. Le Bihan, A. Ustache, and O. Aguerre-Chariol, "Experimental study of the aerosolization of fine alumina particles from bulk by a vortex shaker," *Powder Technology*, vol. 246, pp. 583–589, 2013.
- [41] N. Isbaseta and B. Biscans, "Ultrafine aerosol emission from free fall of TiO₂ and SiO₂ Nanopowders," *Kona*, vol. 25, pp. 190–204, 2007.
- [42] P. A. Baron, A. D. Maynard, and M. Foley, "Evaluation of Aerosol Release during the handling of Unrefined Single Walled Carbon Nanotube Material," NIOSH DART-02-191, 2003.
- [43] A. D. Maynard, P. A. Baron, M. Foley, A. A. Shvedova, E. R. Kisin, and V. Castranova, "Exposure to carbon nanotube material: aerosol release during the handling of unrefined single-walled carbon nanotube material," *Journal of Toxicology and Environmental Health A*, vol. 67, no. 1, pp. 87–107, 2004.
- [44] I. Ogura, H. Sakurai, and M. Gamo, "Dustiness testing of engineered nanomaterials," *Journal of Physics*, vol. 170, Article ID 012003, 2009.
- [45] S. Plitzko, E. Gierke, N. Dziurawitz, and D. Brobell, "Generation of CNT/CNF dusts by a shaker aerosol generator in combination with a thermal precipitator as the collection system for characterization of the fibre morphology," *Gefahrstoffe Reinhaltung der Luft*, vol. 70, no. 1-2, pp. 31–35, 2010.
- [46] T. A. J. Kuhlbusch, C. Asbach, H. Fissan, D. Göhler, and M. Stintz, "Nanoparticle exposure at nanotechnology workplaces: a review," *Particle and Fibre Toxicology*, vol. 8, article 22, 2011.
- [47] A. Thorpe and R. C. Brown, "Measurements of the effectiveness of dust extraction systems of hand sanders used on wood," *Annals of Occupational Hygiene*, vol. 38, no. 3, pp. 279–302, 1994.
- [48] O. Le Bihan, M. Morgeneyer, N. Shandilya, O. A. Chariol, and C. Bressot, *Handbook on Safe Use of Nanomaterials Chapter 7.2: Emission Chambers, A Method for Nanosafety*, Academic Press, San Diego, Calif, USA, 2014.
- [49] B. R'mili, O. Le Bihan, C. Dutouquet, O. Aguerre-Chariol, and E. Frejafon, "Particle sampling by TEM grid filtration," *Aerosol Science and Technology*, vol. 47, pp. 767–775.
- [50] M. George and D. T. Goddard, "The characterisation of rough particle contacts by atomic force microscopy," *Journal of Colloid and Interface Science*, vol. 299, no. 2, pp. 665–672, 2006.
- [51] J. Drelich, "Adhesion forces measured between particles and substrates with nano-roughness," *Minerals and Metallurgical Processing*, vol. 23, no. 4, pp. 226–232, 2006.
- [52] M. S. Esayanur, S. B. Yeruva, Y. I. Rabinovich, and B. M. Moudgil, "Interaction force measurements using atomic force microscopy for characterization and control of adhesion, dispersion and lubrication in particulate systems," *Journal of Adhesion Science and Technology*, vol. 19, no. 8, pp. 611–626, 2005.
- [53] L. J. Jallo, Y. Chen, J. Bowen, F. Etzler, and R. Dave, "Prediction of inter-particle adhesion force from surface energy and surface roughness," *Journal of Adhesion Science and Technology*, vol. 25, no. 4-5, pp. 367–384, 2011.

- [54] W. Q. Ding, "Micro/nano-particle manipulation and adhesion studies," *Adhesion Science and Technology*, vol. 22, pp. 457–480, 2008.
- [55] C. Yuan, Z. Jin, J. L. Tipper, and X. Yan, "Numerical surface characterization of wear debris from artificial joints using atomic force microscopy," *Chinese Science Bulletin*, vol. 54, no. 24, pp. 4583–4588, 2010.
- [56] A. Haris, T. Adachi, and W. Araki, "Nano-scale characterization of fracture surfaces of blended epoxy resins related to fracture properties," *Materials Science and Engineering A*, vol. 496, no. 1–2, pp. 337–344, 2008.
- [57] S. Turri, L. Torlaj, F. Piccinini, and M. Levi, "Abrasion and nanoscratch in nanostructured epoxy coatings," *Journal of Applied Polymer Science*, vol. 118, no. 3, pp. 1720–1727, 2010.
- [58] K. Degiampietro and R. Colaço, "Nanoabrasive wear induced by an AFM diamond tip on stainless steel," *Wear*, vol. 263, no. 7–12, pp. 1579–1584, 2007.
- [59] M. Munz, J.-H. Kim, O. Krause, and D. Roy, "Imaging surfaces of nano-scale roughness by atomic force microscopy with carbon nanotubes as tips: a comparative study," *Surface and Interface Analysis*, vol. 43, no. 11, pp. 1382–1391, 2011.
- [60] R. Holm, *Electrical Contacts*, H. Gerbers, Stockholm, Sweden, 1946.
- [61] T. O. Mulhearn and L. E. Samuels, "The abrasion of metals: a model of the process," *Wear*, vol. 5, no. 6, pp. 478–498, 1962.
- [62] E. Rabinowicz, *Friction and Wear of Materials*, John Wiley and Sons, New York, NY, USA, 1965.
- [63] B. R. Lawn, "A model for the wear of brittle solids under fixed abrasive conditions," *Wear*, vol. 33, no. 2, pp. 369–372, 1975.
- [64] G. Sundararajan, "A new model for two-body abrasive wear based on the localization of plastic deformation," *Wear*, vol. 117, no. 1, pp. 1–35, 1987.
- [65] A. A. Torrance and T. R. Buckley, "A slip-line field model of abrasive wear," *Wear*, vol. 196, no. 1–2, pp. 35–45, 1996.
- [66] U. Olofsson, "Cyclic micro-slip under unlubricated conditions," *Tribology International*, vol. 28, no. 4, pp. 207–217, 1995.
- [67] J. Jiang, F. Sheng, and F. Ren, "Modelling of two-body abrasive wear under multiple contact conditions," *Wear*, vol. 217, no. 1, pp. 35–45, 1998.
- [68] L. Fang, J. Xing, W. Liu, Q. Xue, G. Wu, and X. Zhang, "Computer simulation of two-body abrasion processes," *Wear*, vol. 250–251, no. 2, pp. 1356–1360, 2001.
- [69] S. Fouvry, T. Liskiewicz, P. Kapsa, S. Hannel, and E. Sauger, "An energy description of wear mechanisms and its applications to oscillating sliding contacts," *Wear*, vol. 255, no. 1–6, pp. 287–298, 2003.
- [70] A. A. Torrance, "Modelling abrasive wear," *Wear*, vol. 258, no. 1–4, pp. 281–293, 2005.
- [71] M. T. Siniawski, S. J. Harris, and Q. Wang, "A universal wear law for abrasion," *Wear*, vol. 262, no. 7–8, pp. 883–888, 2007.
- [72] K. De Moerlooze, F. Al-Bender, and H. Van Brussel, "A novel energy-based generic wear model at the asperity level," *Wear*, vol. 270, no. 11–12, pp. 760–770, 2011.
- [73] M. Eriten, A. A. Polycarpou, and L. A. Bergman, "Physics-based modeling for partial slip behavior of spherical contacts," *International Journal of Solids and Structures*, vol. 47, no. 18–19, pp. 2554–2567, 2010.
- [74] M. Eriten, A. A. Polycarpou, and L. A. Bergman, "Physics-based modeling for fretting behavior of nominally flat rough surfaces," *International Journal of Solids and Structures*, vol. 48, no. 10, pp. 1436–1450, 2011.
- [75] M. Kato, A. Tsuruta, S. Kuroda, and Z. Osawa, "Effect of stereoregularity on the photo-oxidative degradation and weathering of polypropylenes," *Polymer Degradation and Stability*, vol. 67, no. 1, pp. 1–5, 2000.
- [76] M. L. Castejon, P. Tiemblo, and J. M. Gomez-Elvira, "Physicochemical processes along the early stages of the thermal degradation of isotactic polypropylene," *Polymer Degradation and Stability*, vol. 70, pp. 297–302, 2000.
- [77] J. Li, R. Yang, J. Yu, and Y. Liu, "Natural photo-aging degradation of polypropylene nanocomposites," *Polymer Degradation and Stability*, vol. 93, no. 1, pp. 84–89, 2008.
- [78] E. Schütz, F. Berger, O. Dirckx, and A. Chambaudet, "Study of degradation mechanisms of a paint coating during an artificial aging test," *Polymer Degradation and Stability*, vol. 65, no. 1, pp. 123–130, 1999.

3. TEST SAMPLE CHARACTERIZATION TECHNIQUES AND PRELIMINARY STUDIES

This section focuses on providing the details about our first preliminary experimental works that were carried out to identify the key parameters in the particle emission and test that whether the findings from the section 2 are feasible to employ or not. Furthermore, details about different characterization techniques are also provided in this section.

During our scientific literature review, it was found that one particular apparatus is frequently being used in different studies for analyzing the performance of products like paint, coating, metal, paper, textile etc., during the application of a mechanical stress. It is widely believed by the researchers (details of the concerned studies are provided later) that this apparatus can simulate the stresses encountered by the surface coatings in a domestic setting, e.g. walking with shoes, displacement of different objects etc. This particular apparatus is called Taber[®] linear abraser (Model 5750; Taber Inc. USA). It is capable to abrade any type of surface (i.e. flat, concave, convex or mix). Its image is shown in figure 3.1 with different features. The abrasion wear is caused by the friction at the contact surface between the surfaces of the mobile abrasant and the stationary test sample placed underneath. The degree of the abrasiveness and hence the abrasion wear can be varied by changing the type of the abrasant and normal load value.

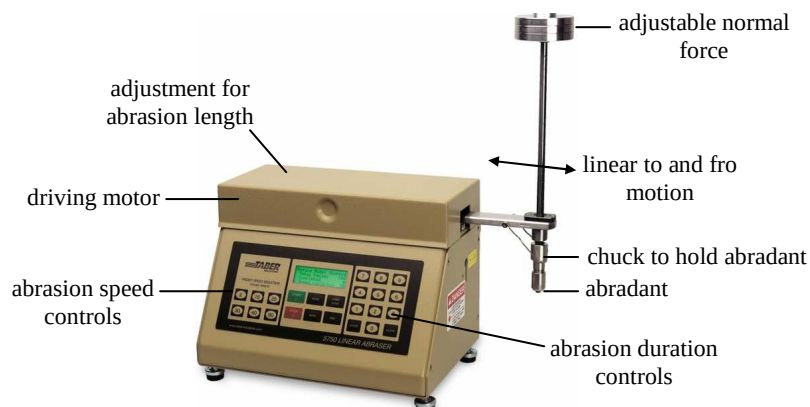


Figure 3.1: Taber[®] 5750 linear abraser (courtesy: Taber Ind.)

It incorporates a motor driven horizontal arm/bar that exerts a Tangential Force on the abrasant and displaces it in a to and fro linear motion over the test sample. Via a vertical shaft, a known weight is mounted on the top of the abrasant which is referred as the Normal Force.

Using this apparatus, a number of preliminary abrasion tests were carried out on several types of traditional or non-nanostructured products that include brittle products like concrete block and masonry bricks, polypropylene polymers, metals like aluminum and steel, and fibrous product like wood.

These traditional products were also characterized before and after the abrasion tests. The characterization techniques involve Scanning Electron Microscopy (QUANTA ESEM[™] 400; FEI Inc. The Netherlands), Transmission Electron Microscopy (TEM; Model CM12; Philips, The Netherlands), Optical Microscopy (Model Imager.M1m; Carl Zeiss MicroImaging GmbH

Germany), Surface tension measurement (Optical Tensiometer; Model Theta; Dyne Technology UK), Energy-dispersive X-ray (EDX; Model X-max; Oxford Instruments UK) and Profilometry (Model 400; Precision Devices Inc. USA).

Based on the experiences from the preliminary studies as well as the pertinent scientific literature (findings of which are provided in section 2), following list of parameters was developed that are believed to play a key role during aerosol particles emission:

- a) **Normal Force:** It is the force which is applied perpendicularly to the direction of the abrasion motion. It is measured in terms of Newton or N.
- b) **Tangential Force:** It is the shear force or the force being applied parallel to the direction of the abrasion motion. It is measured in terms of Newton or N.
- c) **Contact area:** When two bodies touch, a certain portion of their surface areas will be in contact with each other. Contact area is the fraction of this area that consists of the asperities of one surface in contact with the asperities of the other body. Due to the presence of the asperities, surfaces are never perfectly flat. Therefore, the actual contact area (on a microscopic scale) is usually much less than the apparent contact area on a macroscopic scale. Contact area may depend on the normal force between the two bodies due to deformation. It is measured in terms of μm^2 .
- d) **Abrasion speed:** It is the speed at which the abradant displaces over the test sample during abrasion. It is measured in terms m/s or Hertz.
- e) **Surface hardness:** It is a measure of how resistant the surface is to the various kinds of permanent shape change when the normal force is applied. It is measured in terms of Vickers Hardness Number or HV.
- f) **Surface asperities' rms radius:** It is the square root of the arithmetic mean (or average) of the squares of the individual surface asperity radii. It is measured in terms of micrometer or μm .
- g) **Surface roughness:** It is vertical deviation of a real surface from its ideal form. It is measured in terms of micrometer or μm .
- h) **Solid surface tension:** It is the tangential stress (force per unit length) in the surface layer acting as result of the atmospheric pressure and volume stresses inside the body. It is measured in terms of N/m^2 .
- i) **Surface asperities' number density:** It is the number of the surface asperities present in a unit length of the surface. It is measured in terms of $\#/m$.
- j) **Surface Tensile or Young's modulus:** It is a measure of the stiffness of the surface. It is measured in terms of MPa or N/mm^2 .
- k) **Surface Poisson's ratio:** It is the ratio of the transversal to axial expansion of the surface under the combined effect of the normal and tangential forces. It is expressed as a number.
- l) **Standard deviation in the asperity heights distribution:** It is the measure of the amount of variation in the surface asperity heights. It is measured in terms of micrometer or μm .
- m) **Surface yield strength:** It is the stress at which the surface asperities begin to deform plastically. It is measured in terms of N/m^2 .
- n) **Air density:** It is the density of the surrounding air in which the aerosol particles exist. It is measured in terms of kg/m^3 .
- o) **Aerosol particle density:** It is the density of the particles that get generated during abrasion. It is measured in terms of N/m^2 .
- p) **Atmospheric pressure:** It is the pressure of the surrounding air in which the aerosol particles exist. It is measured in terms of Pascals or Pa.

- q) **Surface porosity:** It is a measure of the void spaces in the surface and is a fraction of the volume of voids over the total volume. Its value lies between 0 and 1 with no units.
- r) **Pre-existing crack lengths in the surface asperities:** It is the mean value of all the cracks that already exist in the surface asperities before abrasion. It is measured in terms of μm .

Out of these 18 key parameters, the first two i.e. Normal and tangential forces were studied in further details. By dividing them with the third parameter, i.e. contact area, they are known as the normal and tangential stresses. The motivation for considering these two parameters, in particular, came from the findings of the preliminary studies during which the role of what is known as the mechanical energy input during abrasion was constantly felt to be critical. This energy is also called wear energy. The only way to quantify the wear energy is by measuring the normal and tangential forces. Thus, the importance of the wear energy directly implies the importance of the normal and tangential forces. In this section, one of the preliminary studies is shown through a research article, entitled “Investigation of the release of particles from a nanocoated product”. It investigates the release of nanoparticles during the operations related to the handling of and processing of a nano-coated automobile shaft cap. For different levels of wear energy, concentration levels of emitted particles in air have been measured. For the given wear energy levels, an increase in particle emission increases was found with the increase in the wear energy. The detailed studies on the normal and tangential forces are mentioned later in the sections 4 and 5 respectively.

Hence, by performing different preliminary experimental studies (like the one shown here) we were able to identify various key parameters in the particles emission. However, one cannot be sure that if this list is exhaustive or not.

Since the key parameters have been identified, therefore, at this moment, we need to develop an experimental set-up which allows us to measure the effect of the variation of these key parameters on the emission, especially in the case of the two forces. This is discussed in the section 4.

Investigation of the Release of Particles from a Nanocoated Product

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ABSTRACT

Manufactured products are being coated with nanoparticles in order to functionalize them with antibacterial or self-cleaning properties or to improve their durability etc. As the (eco-) toxicological effects of the nanoparticles are not well known yet, their use could lead to new potential risks for the workers, the consumers and the environment. This study focuses on the release of the nanoparticles during the operations related to the handling and processing of an automotive part. The part is made up of a metallic alloy and, in order to reduce friction, the part is nano-coated with inorganic fullerenes. The mechanical stresses appearing during these operations are reproduced in a nano-secured facility. The release of nanoparticles is found to be increasing with the wear energy applied on the surface.

Keywords: Nanoparticle; Coating; Emission; Wear; Friction; Release

1. Introduction

There is a growing interest in the development of nano-coatings in industrial applications. The finished products, once nano-coated, can be self-cleaning, antibacterial, UV-resistant etc. Due to these advantages, their usage is becoming frequent and thus, subjected to investigations regarding the release of nanoparticles (NP) in the air, which may pose toxicological effects on the human and the environment. These effects of NPs are not well known yet and represent thus a possible threat, especially, since a new era of this new technology is commencing hastily. During their whole life-cycle, the products are exposed to wear by their environment and utilization and thus degradation might occur, [1-3] which could lead to the release of NP. However, in view of the large variety of possible exposures, the present data are still not sufficient. Moreover, as workplace atmosphere inspection for manufactured nanoparticles is relatively complex and expensive to conduct, new comprehensive studies may be required to provide estimates of their release in the occupational exposure. The need for these studies will rapidly increase due to growing production and use of manufactured nanoparticles. Previous studies (**Table 1**) have shown the emission of particles from different types of materials when solicited mechanically or thermomechanically or by UV. For environmental degradation,

it has been shown that exposure to UV radiations can lead to the increase of the density of NPs on the surface of a nano-structured polymer composite [3]. Fewer works have studied the exposure risks during handling and operating nanoparticles [4]. But new heights have been achieved when the nanoparticles were started being characterized during their generation process through wear. Their characterization also got encouraged with the fact that in several cases of mechanical wear, very high particle emissions have been observed for nanostructured materials, e.g. when drilling, [5] grinding, [6] or sanding [7] (see **Table 1**). From comparisons of materials with and without nano-structure, it has been confirmed that emission of particles occurs in both cases [5,7]. The study presented here aims at characterizing a possible source of NP release to air, which may lead to their inhalation and thus the possible worker exposure to NP during the operations related to the handling and processing of an automotive nanocoated part. Analysis has been carried out to quantify and characterize the particle emission levels of the part during the subsequent wear processes. An attempt, simulating these wear processes in real life conditions experimentally, is presented.

2. Experiments

For the experimental investigation, an iron alloy shaft cap with a radius of 2 cm and height 5 cm was used. Its

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Table 1. Overview of references.

Material	Wear mechanism	Particle emission		Reference number
		Total number concentration and size range	Main observations and findings	
Coated surfaces with zinc oxide nanoparticles	Abrasion with a Taber	<20 particles/cm ³ [6 nm - 1 µm]	The total number of generated submicrometer or nanoparticles was extremely low and lay below the statistic significance threshold. The particles <100 nm remain embedded in the coarse wear particles.	[10]
Polycarbonate containing 3% wt Carbon Nanotube (CNT)	Abrasion with a Taber	50 - 1800 particles/cm ³ [7 nm - 10 µm]	The abrasion effect is enhanced when increasing the normal force. The particle emission is also increased with the speed (number of cycle per minute). No free CNTs were observed.	[8]
Polymethyl Methacrylate (PMMA) containing 10% wt Cu	Abrasion with a Taber	Up-to 10,000 particles/cm ³ [7 nm - 10 µm]	The type of abrasion tool has a high impact on particle emission intensity. No visible free Cu nanoparticles were observed even for one case they would be nearly released.	[9]
TiO ₂ nanopowder coated on different substrates including wood, polymer and tile.	UV + fan + rubber knife	~10 to 600 particles/cm ³ [15 - 661 nm]	These actions together can greatly reduce the binding force between the TiO ₂ nanopowder and the substrate surface, and, therefore produce particle emissions from the coating products.	[15]
Paints with or without engineered nanoparticles (NP). NP: carbon black and TiO ₂	Sanding	14,000 - 28,000 particles/cm ³ [5 nm - 20 µm]	The sander was the only source of particles smaller than 50 nm and they dominated the number concentration spectra. NPs released during the sanding do not occur in individual particles.	[7]
Non-nanodoted materials: Granite, Ceramic, Steel, Aluminum, PTFE, Hardwood	Grinding	10,000 - 800,000 particles/cm ³ [4 nm - 20 µm]	Ultrafine particles do have the potential to form a significant component of a grinding aerosol for a number of substrates. processes: 1) from within the grinding motor, 2) from the combustion of amenable grinding substrates and 3) from volatilization of amenable grinding materials at the grinding wheel/substrate interface.	[6]
Surfboard with or without carbon nanotubes (CNT)	Drilling and grinding	Upto 107 particles/cm ³ [7 nm - 10 µm]	When used, the CNT are not placed in the outside layer, but inside. Material with or without CNT: the particle emissions are comparable. The top layer (varnish) is the major source of particles.	[5]
Steel and fiber cement panels coated with the ZnO and Fe ₂ O ₃ nanoparticles	Sanding	Upto 109 particles/cm ³	For the given stress, the swarf mass, the particle size distribution of the released aerosol, and consequently the number of released particles depend primarily on the used surface coating.	[11]
Epoxy nanocomposites reinforced with CNTs	Weighing operation and sanding	With no local exhaust ventilation: 2.68 µg/m ³ Inside the fume hood: 21.4 µg/m ³	This study demonstrated that weighing bulk CNTs and sanding epoxy containing CNTs generate few airborne particles that are nano-sized. Furthermore, it was demonstrated that sanding epoxy containing CNTs may generate micrometer-sized particles with CNTs protruding from the main particle core.	[12]
PA6 nanocomposites	Drilling	20,000 particles/cm ³ [175 and 350 nm]	It is likely that the presence of nanoclay in some way retains the formation of high quantity of airborne particles and promotes particle deposition.	[13]
Concrete	Cutting	5.28 ± 1.26 mg/m ³	An increase in CS resulted in an increase in the four measured particle exposure levels resulting from its influence on the generation of coarse particles. For both Ctho and Cres which are known to have a higher content of fine particles, the increase in AF resulted in an increase in their concentrations. However, for the concentrations with a higher fractions of coarse particles (<i>i.e.</i> , Ctot and Cinh), the increase in AF led to an initial increase, followed by a decrease in measured particle exposure concentrations.	[14]

surface was coated homogeneously with inorganic fullerene, having a coating thickness of 0.1 µm. The coating ensures the lowering of its friction coefficient. An emission chamber *i.e.* a sealed glove box (model 830-ABC/EXP, Plas-Labs), has been used to ensure lim-

ited background particles concentration inside the chamber and to prevent the release of (nano) particles to the outside atmosphere, thus, providing a nano-secured facility. The details of all the instruments, used during the test, are given in **Table 2**. During the whole test, clean air

Table 2. Instrumentation.

Parameter	Technique	Instruments	Characteristics	Set sample time
Number concentration [4 nm - 1 μm]	Condensation Particle Counter (CPC)	TSI model 3785	Water-based	1 s
		Grimm model 5.400	Butanol-based	6 s
Size distribution [10 nm - 0.5 μm]	Scanning Mobility Particle Sizer (SMPS)	DMA TSI model 3081 + CPC TSI model 3010		235 s
Size distribution [0.3 - 20 μm]	Optical Counter (COP)	Grimm model 1.108		6 s

(Filtered Air Supply 3074B, TSI) is passed upwards through the chamber. All devices are fed from a unique sampling point, which is set above the testing part to collect the maximum of particles released into the air from the experiment (**Figure 1**). The clean air inlet flow rate is equal to 0.075 lps. It enhances to carry out the investigation in an atmosphere practically free of particles (2 particles/cm³) and thus to detect emitted particles even at the low emission levels. Two Condensation Particle Counters—water based CPC (model 3785, TSI) and a butanol-based CPC (model 5.400, Grimm)—have been used in parallel which enabled reliable measurements of even low particle number concentrations, in the range of particle sizes from 4 nm to 1 μm . The particle size distribution is measured by a Scanning Mobility Particle Sizer (SMPS) configured with a long Differential Mobility Analyzer (DMA, model 3081) for particles' size ranging from 10 nm to 500 nm and by an Optical Particle Counter (OPC, model 1.108, Grimm) for particles' size ranging from 300 nm to 20 μm . The total sample time for SMPS has been kept at 235 s (scan time 215 s, retrace time 20 s) whereas for other instruments, it has been kept at low values. For validating the scan by SMPS, it was operated only under stable particle concentration conditions. However, a rougher state of the particles concentration stability cannot be neglected and excluded from the scanning period in these types of experiments. The experimental investigations presented here are corresponding to the operations which occur when a part, under development, is handled e.g. for unpacking, roughness measurement, specimen preparation for microscopy observations and other tests. In order to simulate these real life operations at real scale, following experiments have been carried out sequentially on a given part with increasing levels of stresses: 1) Extraction from the safety bag; 2) Plastic bag agitation; 3) Part extraction from plastic bag; 4) Part moves in 3 dimensions; 5) Surface rubbing with glove; 6) Falling from a height of 20 cm; 7) Surface scratching in 3 directions; 8) Surface sawing; 9) Surface sanding. The sampling point to measure the particles number concentration has been kept in the vicinity of the source. All the above mentioned operations were carried out in a glove box measuring 300 cm $\times$ 240 cm $\times$ 360 cm. For test #9, the rotary tool's

motor (Dremel 400 DIGITAL with a rotating aluminum oxide abrasive wheel) has been placed outside the chamber to avoid the contamination from the particles released by the motor's brushes. Its velocity of rotation has been kept at 19,000 rpm. It is interesting to note that these activities are also arranged in ascending order of wear energy levels. The wear energy associated with a system in a process can be defined as the energy consumed during machining or erosion or deterioration of the system during that process. The precautions for nanosafety are achieved by placing the glove-box within a nanosecured venting hood and putting the sample parts into two plastic bags, when not in use. However, due to the lack of the information on homogenization of the inside air due to ventilation, inlet and exhaust valves, data available on the measure of the particles number concentration should be considered as semi-quantitative. In order to ensure the repeatability of data and results presented in the present work, the whole experimental procedure was repeated three times. The particle deposition on the surface walls is a critical issue in such experiments which are done in a confined area. This may lead to the carrying out of these particles from one experimental trial to another. An utmost care has been taken to avoid it by cleaning the surface walls using an ethanol absorbed paper after every test and trial.

3. Experimental Results

The number concentration of the released particles versus time, measured by means of COP Grimm, water based CPC and butanol based CPC, in a sequential order, is shown in **Figure 2**. Note that **Figure 2** depicts the number concentration during one of the three trials. The particle concentration level appearing before applying any stress (often referred as background noise level) is approximately 2 particles/cm³. During test #1, *i.e.* extraction of the part from its bag, a particle concentration of 4 particles/cm³ was measured. Tests #2 to #7 generate peaks of particle concentration of approximately 10 particles/cm³, while peaks for sawing (test #8) range from 50 to 1000 particles/cm³. Test #9 generates highest concentration level of 900 particles/cm³ which is measured for the particles lying in a size range of 10 nm to 0.5 μm , as shown in **Figure 3**. From **Figure 3**, it is evident that

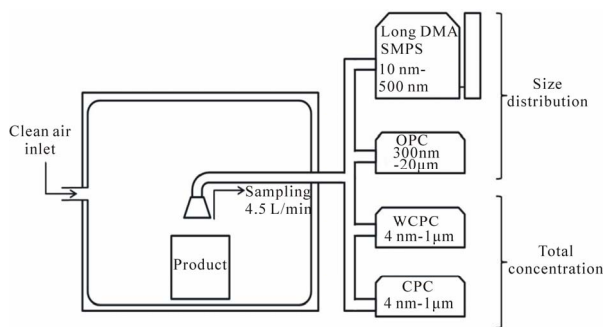


Figure 1. Experimental set-up.

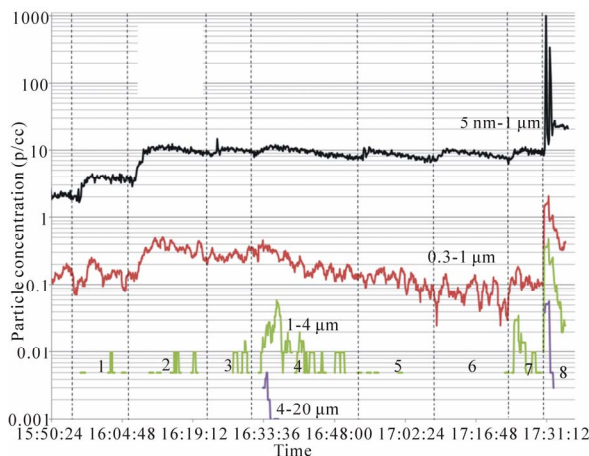


Figure 2. Particle concentration through time for different size ranges while testing a single nanocoated part (cf. Table 3, except sanding).

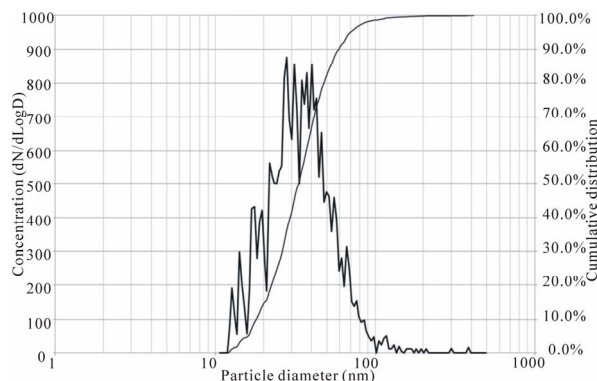


Figure 3. Particle size distribution while sanding measured by SMPS.

50% of the particles generated during sanding are smaller than 40 nm.

During tests #1 to #5, the wear energy levels are very low due to low level of stress application. For the particles lying in the size range of 5 nm to 1 μm , their concentrations were found to be in the range of 4 to 12 particles/ cm^3 . For micron sized particles, concentration levels are also low. Therefore, from these observations, it has been found that for the present nanocoated shaft cap,

handling operations (tests #1 to #5) do not involve any particle emission or their exposure threats to the operator. However, for the tests #6 to #9, there may be possibility of a considerable particle emission because of the involvement of high levels of stress application. However, for tests #6 and #7, this hasn't been seen so far. The only phase where a significant emission has been seen is test #9. In this test, as soon as the sanding commences, there occurs a sharp peak of the number concentration due to the ejection of the particles from the material. To have a stable particle concentration during the particles size scanning by SMPS, the scan starts after the peak has arrived and it starts diminishing slowly with time, thus, providing a rough but stable particles presence.

4. The Energetic Approach

In the present approach, we have seen a series of operations involving increasing order of stresses acting on the nano-coated part. For the handling operations involving low stresses (#1 to #5), the particles emission is negligible. For the test #6, which involves accidental fall of the part, the same low emission continues. In order to get a better insight of this accidental scenario, the type of material in play should be noted. This is a light weight iron alloy which has got a high value of impact strength and ductility. The impact stress to which it is subjected at the end of the fall was calculated and found to be less than 100 Pa Equation (1) which is very less in magnitude as compared to its material impact strength. This means, all the impact applied on this nano-coated part gets sufficiently absorbed by rendering the part untouched. As a result, the wear energy applied on this part seemed to be lesser than required in order to have a higher particles emission. But if the same wear energy had been applied on a brittle material having very low impact strength (ex. Ceramics, concrete, glass etc.) the scenario of accidental fall would have produced high particles emission concentration. Therefore, it shows that the particles emission depends on both the wear energy level as well as the material to which it is being applied. For test #7, the low particle emission concentration during the peeling off of nanocoating signifies the sustainability of integrity of nanocoating during getting peeled off. However, it still requires a better view on structural changes occurring during this process. In **Table 4**, the values of wear energy are shown with their corresponding total particle number concentrations. For the calculation, following basic equations have been employed:

For accidental fall:

$$E_a = m * g * h \quad (1)$$

For scratching and sawing:

$$E_d = \mu * F_N * d \quad (2)$$

Table 3. Stress tests-description, aim and results.

#	Description	Aim	Wear Energy level	Total Particle emission concentration (#/cm ³)			
				5 nm - 1 µm	0.3 - 1 µm	1 - 4 µm	4 - 20 µm
1	Extraction from the safety bag		Very low	2	~0	~0	~0
2	Plastic bag agitation	Nanoparticles release while handling the part	Very low	10	<1	~0	~0
3	Part extraction from plastic bag		Very low	10	~0	~0	~0
4	Part moves in 3 dimensions + shock test		Very low	10	~0	10	+
5	Surface rubbing with glove	Accidental scenario #1	Very low	10	~0	~0	~0
6	Falling from a height of 20 cm (h)	Accidental scenario #2	Low	10	~0	~0	~0
7	Surface scratching (3 directions)	Nanoparticles release during roughness measurement	Low	12	<1	~0	~0
8	Surface sawing	Nanoparticles released during sample preparation for microscopy	Medium	300	2	<1	<1
9	Surface sanding	Extreme stress	High	100,000	X	X	X

For sanding:

$$E_d = \mu * F_N * r * \omega * t \quad (3)$$

with E_a is the energy absorbed (J), m is the mass (kg), g is the acceleration due to gravity (m/s²), h is the height of the fall, E_d is the energy loss (J), F_N is the normal load (N), d is the crossed distance (m), μ is the friction coefficient, r is the radius of the abrasive wheel (m), ω is the velocity of rotation (rad/s) and t is the stress duration (s). In **Figure 4**, the wear energy levels applied on the nano-coated part have been plotted on a log-log graph. The four points in the **Figure 4** correspond to the four energy levels in the tests #6 to #9. Clearly, with increasing wear energy level, particles emission concentration also increases, hence a direct proportionality between the two.

5. Discussions and Conclusions

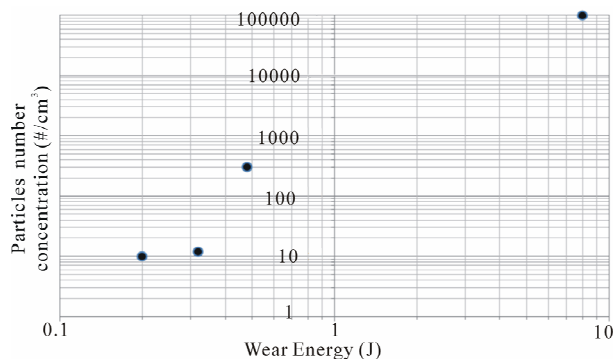
The study presented here investigates the release of nanoparticles during the operations related to the handling of and processing of a nano-coated shaft cap. For different types of wear, concentration levels of emitted particles in air have been measured. The whole experimental procedure was divided in nine carefully selected tests and done in a proper nano-secured facility. Using state of the art instrumentation, concentration and size levels of the emitted particles were quantified. There was no significant particle release during the handling operations (tests #1 to #6). There has been a presence of low concentration of micronic particles for the nano-coated part during tests #2 and #4. These results were also compared with the results obtained from a same part but uncoated. No considerable difference was observed between the two except for the test of surface scratching.

During the sanding test (#9), it has been found that the total number concentration of the released particles has been dominated by the nanoparticles with a mean diameter size of 35 nm. This conclusion agrees with the results of Koponen *et al.*, 2009 and Göhler *et al.*, 2010. This should be noted that because the aerosol was sampled directly in the vicinity of the particle generation source, the measured particle numbers represent maximum possible values in a practical case. The concept of wear energy has been introduced to the present study. It has proved to be a valuable indicator for forecasting the behavior of particles' emission. From the trend observed during experimental conditions, it may be suggested that with wear energy, particle emission increases. With the use of primary force-energy relationships, wear energy has been approximated and was found to be showing a positive correlation with particle emission. However, this hypothesis still needs more experimental trials to get verified.

Although the present study itself provides some of the valuable information on the particle emission behavior, it still demands both an improved energy model as well as refined experimental setup to understand the particle-energy interaction at microscale. The wear energy calculation must take into consideration that the frictional force is not a constant term. For the present study, there were limited number of test samples but authors will follow the work with more samples in order to provide a versatile asset to this study. As seen in the study, there has either been very weak release of the nanoparticles during handling operations or a strong release at higher energy levels. Therefore, in between these two extreme states, more sophisticated experimental procedures are

Table 4. Wear energy and particle emission associated with tests #6 to #9.

Test	Wear energy (J)	Total particle number concentration (#/cm ³)
Accidental fall	0.2	10
Scratching	0.32	12
Sawing	0.48	300
Sanding	8	100,000

**Figure 4. Total particle concentration versus dissipated energy.**

required to set and measure the applied wear energy. To verify the emissions and their characteristics, the scanning electron microscopy and chemical analysis of the fullerenes are required which will be followed in the subsequent work.

6. Acknowledgements

The authors wish to thank the French Ministry of Ecology and the European project FOREMOST for the financial supports of this study.

REFERENCES

- [1] AFSSET (2010) "Évaluation des Risques Liés aux Nanomatériaux Pour la Population Générale et Pour l'Environnement," Saisine No. 2008/005, Rapport d'Expertise Collective, 2010.
http://www.afsset.fr/upload/bibliotheque/460552230101468097041324565478/10_03_ED_Les_nanomatériaux_Rapport_comprime.pdf
- [2] L. Reijnders, "The Release of TiO₂ and SiO₂ Nanoparticles from Nanocomposites," *Polymer Degradation and Stability*, Vol. 94, No. 5, 2009, pp. 873-876.
[doi:10.1016/j.polymdegradstab.2009.02.005](https://doi.org/10.1016/j.polymdegradstab.2009.02.005)
- [3] T. Nguyen, et al., "Fate of Nanoparticles during Life Cycle of Polymer Nanocomposites," *Journal of Physics: Conference Series*, Vol. 304, No. 1, 2010, Article ID: 012060.
- [4] T. Schneider, D. H. Brouwer, I. K. Koponen, K. A. Jensen and W. Fransman, B. Van Duuren-Stuurman, M. Van Tongeren and E. Tieleman, "Conceptual Model for Assessment of Inhalation Exposure to Manufactured Nanoparticles," *Journal of Exposure Science and Environmental Epidemiology*, Vol. 21, No. 5, 2011, pp. 450-463.
[doi:10.1038/jes.2011.4](https://doi.org/10.1038/jes.2011.4)
- [5] O. Le Bihan and K. Schierholz, "Assessment of Nanoparticles Emission from Manufactured Products: Feasibility Study," *Proceedings of Nanosafe 2008: International Conference on Safe Production and Use of Nanomaterials*, Grenoble, 3-7 November 2008.
- [6] A. Zimmer and A. Maynard, "Investigation of the Aerosols Produced by a High-Speed, Hand-Held Grinder Using Various Substrates," *Annals of Occupational Hygiene*, Vol. 46, No. 8, 2002, pp. 663-672.
[doi:10.1093/annhyg/mef089](https://doi.org/10.1093/annhyg/mef089)
- [7] I. K. Koponen, K. A. Jensen and T. Schneider, "Sanding Dust from Nanoparticle-Containing Paints," *Journal of Physics: Conference Series*, Vol. 151, No. 1, 2009, Article ID: 012048.
- [8] L. Golanski, A. Guiot, D. Braganza and F. Tardif, "New Method for the Characterization of Abrasion Induced Nanoparticle Release into Air from Nanomaterials," *Proceedings of Nanotechnology*, 2010.
http://materiales.azc.uam.mx/area/Ingenieria_Materiales/investigaci%C3%B3n/2261204/cuan%20calif/Cuan%20TechConWo2010/CD/Nanotech2010/pdf/905.pdf
- [9] A. Guiot, L. Golanski and F. Tardif, "Measurement of Nanoparticle Removal by Abrasion," *Journal of Physics: Conference Series*, Vol. 170, No. 1, 2009, Article ID: 012014.
- [10] M. Vorbau, L. Hilleman and M. Stintz, "Method for the Characterization of the Abrasion Induced Nanoparticle Release into Air from Surface Coatings," *Aerosol Science*, Vol. 40, No. 3, 2009, pp. 209-217.
- [11] D. Göhler, M. Stintz, L. Hillemann and M. Vorbau, "Characterization of Nanoparticles Release from Surface Coatings by the Simulation of a Sanding Process," *Annals of Occupational Hygiene*, Vol. 54, No. 6, 2010, pp. 615-624.
[doi:10.1093/annhyg/meq053](https://doi.org/10.1093/annhyg/meq053)
- [12] L. G. Cena and T. M. Peters, "Characterization and Control of Airborne Particles Emitted during Production of Epoxy/Carbon Nanotube Nanocomposites," *Occupational and Environmental Hygiene*, Vol. 8, No. 2, 2011, pp. 86-92.
[doi:10.1080/15459624.2011.545943](https://doi.org/10.1080/15459624.2011.545943)
- [13] S. Sachse, F. Silva, H. Zhu, A. Irfan, A. Leszczynska and K. Pielichowski, "The Effect of Nanoclay on Dust Generation during Drilling of PA6 Nanocomposites," *Journal of Nanomaterials*, 2012, Article ID: 189386.
[doi:10.1155/2012/189386](https://doi.org/10.1155/2012/189386)
- [14] J. C. Soo, P. J. Tsai, C. H. Chen, M. R. Chen, K. I. Hsu and T. N. Wu, "Influence of Compressive Strength and Applied Force in Concrete on Particles Exposure Concentrations during Cutting Processes," *Science of the Total Environment*, Vol. 409, No. 17, 2011, pp. 3124-3128.
[doi:10.1016/j.scitotenv.2011.05.016](https://doi.org/10.1016/j.scitotenv.2011.05.016)
- [15] L. Y. Hsu and H. M. Chein, "Evaluation of Nanoparticles Emission for TiO₂ Nanopowder Coating Materials," *Nanoparticle Research*, Vol. 9, No. 1, 2007, pp. 157-163.

4. EXPERIMENTAL SET UP

This section details the experimental setup which was developed on the basis of the experimental observations during preliminary abrasion tests and can sufficiently measure the key parameters enlisted in the section 3. Moreover, it was also tested to ensure that the results of the aerosol particles emission during abrasion are reproducible.

Two key features of this experimental set-up are:

- (i) measurement and control of the full mechanical stress or force state (i.e. measurement and control of the normal and tangential stresses or forces) acting during abrasion which had been made possible by considering an instrumentally modified form of the Taber linear abraser, the standard form of which was initially used for performing preliminary abrasion tests and couldn't do this.
- (ii) both qualitative as well as semi-quantitative analysis of the emitted aerosol particles in real time. In the qualitative analysis of the emitted aerosol particles, one may determine their shape and elemental composition. In the semi-quantitative, one may determine their number and size with some particle losses*.

The biggest advantage of the first key feature is that one may now reproduce the stress conditions which act during any real life activity in a laboratory scale experiment. Thus, by combining this feature with the second one, one may assess the aerosol emission tendency of any real life mechanical stresses application activity on any potential aerosol particles emission source.

The following research article, entitled “Use of a modified Taber abrasion apparatus for investigating the complete stress state during abrasion and in-process wear particle aerosol generation”, discusses all these aspects in details through an illustration of the experimental set-up (figure 3 in the article).

* Particle losses in the present experimental set-up can be due to their deposition on the walls of emission test chamber or tubes that transport them from this chamber to the particle sizers and counters. By using a moderate sized radial symmetric sampling hood of volume equal to 713 cm³, the particles loss due to their deposition on the emission test chamber walls can be minimized. With respect to the losses in tubes, their estimation attempt was made by considering five major phenomena which render these losses: **(i)** gravitational settling **(ii)** diffusional deposition **(iii)** turbulent inertial deposition **(iv)** inertial deposition at a tube bend **(v)** inertial deposition at flow constrictions.

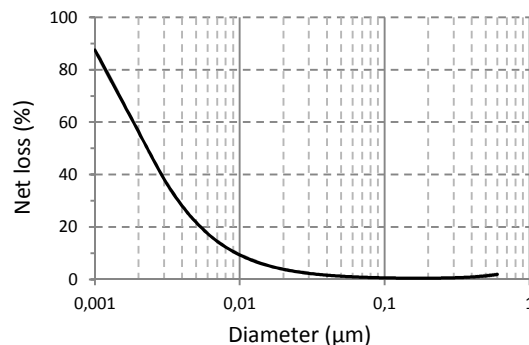


Figure 4.1: Estimation of the particle losses in the tubes for the present experimental set-up

In figure 4.1, the net loss percentage of the particles (due to these five phenomena) has been shown as a function of the particle size for the lengths and orientations of the tubes used during connection in the present experimental set-up. The simplified equations, formulating these losses, are presented in the “Appendix” of the article on page 45. For more details on these loss mechanisms, the readers are encouraged to refer to Kulkarni P. et al., *Aerosol Measurement: Principle, Techniques and Applications*, 2011

It talks about different aspects of the instrumental modification of Taber abraser, including its mounting, calibration and final validations. It further justifies the selection of the tangential force as a principle key parameter during emission by showing the material removal mechanism during abrasion and the emission of aerosol particles to be its function. During some case studies which were done using this instrument only, it also shows that how it can be useful in various types of material related applications.

It is worth to mention here that in the figure 3 of this research article, there is an element called *Emission Test Chamber*. The main aim of this chamber is to differentiate and isolate the particle aerosols released during abrasion from omnipresent background particles. It is important to do because commonly used equipments for aerosols measurement only physically characterize aerosols and do not distinguish between background and released particle aerosols.

In order to provide further details on this important element of the experimental set-up, a book chapter, entitled “Emission Chambers- A method for nanosafety”, is provided after the research article. This chapter gives recommendations for systematic studies on possible particle aerosols release under different stress situations. The use of emission chambers with very low background noise is recommended. It further summarizes the findings of different experimental studies in the literature that have used such chambers to study the release of ENM from nanostructured products under various stress conditions, e.g., abrasion, UV irradiation, etc.

Since the experimental set-up developed here can measure the key parameters with required certainty and observe easily their variation effect on the emitted aerosol particles, it is now time to employ it for testing the commercial nanostructured products for their nanoparticles emission tendency during abrasion. The results are shown in the section 5.



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Short communication

Use of a modified Taber abrasion apparatus for investigating the complete stress state during abrasion and in-process wear particle aerosol generation

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A B S T R A C T

A present challenge in chemical nano-product formulation is the prediction of structure–function relationships of designed nano-particle based chemical engineering products such as coatings or solids. A particular attention is in this framework today paid to the question whether such products will release particles to the air during their life cycle. This aerosolization of (nano-) particles impacts possibly occupational and consumer health. A possible particle release mechanism here is simply wear, i.e. for example when holding, moving or walking on nano-functionalized products. This means that further to the study of aerosolization, today's chemical engineers need to be able to study wear, enabling them to make future products 'nanosafe by design'.

The present article presents an affordable option for knowing the complete stress state, including both normal and tangential stresses, acting during alternated sliding abrasion when measuring the response of a surface to its wear. For this, a standard TaberTM linear abrasion 5750 apparatus is modified by adding a strain gauge and further coupled with a particle counter and particle sizers for quantifying the release of wear particles in air during abrasion. After the calibration, the modification is validated by comparing the force measurements with that of a commercial tribometer. Different case studies which were carried out using this modified apparatus show (i) clearly visible static and dynamic friction ranges and (ii) clear dependency of the wear behavior and the particle aerosolization on the chosen couple material–abraser.

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Keywords: Nanosafety by design; Friction; Wear; Debris; Aerosol; Tribometer

1. Introduction

Since the introduction of the Taber abrasion apparatus in 1930s, it has become a popular instrument for evaluating abrasion and wear resistance of a wide spectrum of materials

(including plastics, coatings, laminates, leather, paper, ceramics, carpets, safety glazing, etc.) (Shandilya et al., 2014a). Easy to operate, the instrument is also referenced in numerous internationally recognized test standards (ASTM, 1996, 2007, 2008). With no limitation on the nature of surface (i.e. flat,

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concave, convex or mix), there is no limit on the sample sizes too. Moreover, its reasonable cost makes it affordable for small scale enterprises and research laboratories. Owing to a robust design, there have been some attempts in the past to modify this standard abrasion apparatus. For instance, the decreasing protection of organic coatings was measured by Rossi et al. (2006) by establishing an electrical contact between the test sample and the electrochemical equipment. Similarly, for compensating small unevennesses during sliding wear, Riestler et al. (1997) connected the sliding horizontal bar of the Taber apparatus to a spring.

Apart from these modifications, the aerosolization or the release of wear particles in air during abrasion is also one of the sought after research topics these days (Golanski et al., 2012; Vorbau et al., 2009; Gohler et al., 2010; Schlagenhauf et al., 2012). All these studies have used the Taber abrasion apparatus in its standard form for carrying out abrasion. Since its standard form allows for setting a normal abrasion stress but not for knowing the resulting tangential stress, any chance of determining the role of the abrasion stress state during particle aerosolization is obscured in these studies.

Therefore, in the present work, two aspects have been targeted:

- (i) the insufficiency of a standard Taber 5750 linear abrasion apparatus to determine the complete stress state (i.e. measurement of the tangential stress in addition to setting the normal stress) existing during linear sliding abrasion and
- (ii) preliminary assessment of the role of the stress state in the particle aerosolization.

As a result, we have equipped the standard Taber abrasion apparatus with a strain gauge and further coupled it with particle counter and particle sizers. By using this, the determination of the stress state and quantification of the wear particles getting generated and released in air during abrasion can be done simultaneously. Such a modification is discussed here using its description, calibration and preliminary case studies.

2. Theory

In widely used approaches based on contact mechanics for finding the wear volume generated during abrasion, the Archard approach, i.e.

$$v = \frac{kF_N L}{H} \quad (1)$$

is applied (Hegadekotte et al., 2008; Meng and Ludema, 1995). It relates the wear volume, v (in m^3), to the product of the sliding distance, L (in m), and the normal load, F_N (in N). In Eq. (1), k is a dimensionless constant and H (in MPa) is the hardness of the worn material. However, this approach assumes a constant friction coefficient during alternated sliding motion which is not the case in reality (Shandilya et al., 2014b). In such a case, it appears to be much more relevant to consider the wear energy (E_W) as a significant wear parameter (Fouvry et al., 2003).

$$E_W = F_T L \quad (2)$$

In Eq. (2), F_T (in N) is the tangential force acting during abrasion. One can define E_W as the energy dissipated during wear yielding new surfaces and particles (Le Bihan et al.,

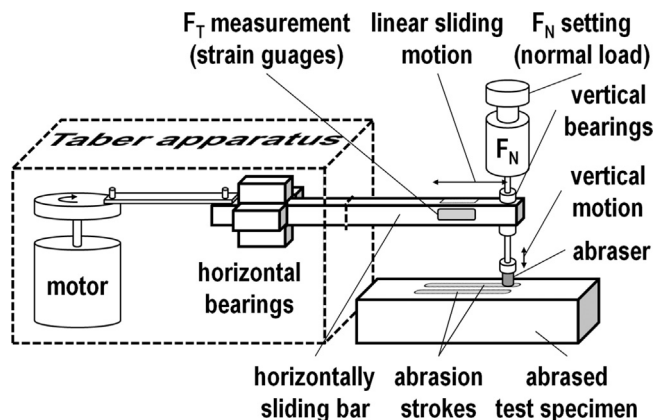


Fig. 1 – Schematic of the working and loading conditions of a std. Taber apparatus.

2013; Shandilya et al., 2013). E_W may provide valuable information leading to a better understanding to the wear process and wear mechanisms (Hokkirigawa and Kato, 1988). While modeling a two body abrasive wear, Jiang et al. (1998) have shown that the E_W is lower for the cutting or fracturing like material removal phenomenon while it holds a higher value when the surface wears through plastic deformation. Apart from this, E_W finds itself playing a key role in the study of the aerosolization of particles during abrasion wear too. Various studies have demonstrated that the abrasion wear of the surfaces is accompanied by the aerosolization or release of wear particles in air (Golanski et al., 2012; Vorbau et al., 2009; Gohler et al., 2010; Le Bihan et al., 2013; Shandilya et al., 2013). Some have concluded that the concentration of the wear particles aerosol depends directly on E_W (Le Bihan et al., 2013; Shandilya et al., 2013). From Eq. (2), for calculating E_W , the knowledge of F_T becomes indispensable.

3. Developed method

3.1. Normal and tangential force measurement

The standard Taber linear abrasion apparatus (Model 5750; Taber Inc., USA) incorporates a horizontal arm/bar that reciprocates in a linear motion. Fig. 1 presents a schematic diagram. A precision roller bearing carrying spline shaft is attached at the end of the bar that allows a free-floating vertical motion of the abramer (fixed in a spline shaft using a mandrel) over the test specimen which is affixed to the bottom.

The weight support is mounted on the top of the shaft which is used to add a known weight (F_N) in normal direction (direction $-z$ in Fig. 1) to the plane of the sliding motion, i.e. plane $x-y$. In the standard version of this apparatus, an unknown force is applied horizontally (F_T) through a motor. The method developed in the present work for knowing F_T has two principal steps: (i) replacement of the original stainless steel horizontal bar with a replica in aluminum and (ii) mounting a strain gauge on the top surface of this replicated aluminum bar.

Fig. 2 illustrates these two aspects. The element 1 in Fig. 2 represents the replicated horizontal bar of Aluminum 2024 alloy. This material is known for its good machinability (i.e. ease of reproducing the exact dimensions as that of the original steel bar installed in the standard version of the Taber apparatus) and fatigue resistance (i.e. resistance to the deformation due to long term continuous cycles). The mechanical

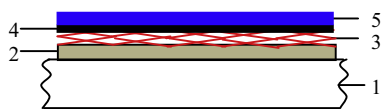


Fig. 2 – Layout of the strain gauge mounted on the top surface of the horizontal bar (1 – horizontal bar (aluminum), 2 – adhesive, 3 – bonding aid, 4 – strain sensor foil, and 5 – protective paint).

properties of this alloy are as follows: Yield strength – 140 MPa; Young's Modulus – 73 GPa and Poisson's ratio – 0.42. The *element* 2 is a cold curing adhesive called Z70 which is basically a single component adhesive Cyanoacrylate thin liquid. It bonds the SG with the aluminum bar. The *element* 3 is a bonding aid (thickness: 0.05 mm; width: 60 mm) which prevents other material except SG from bonding to the bar. The *element* 4 is a SG (LY13-1.5/350; HBM GmbH, Germany) having 1.5 mm of active measuring grid length and 5.7 mm of measuring grid carrier length. It is made of a constantan foil having $3.8\ \mu\text{m}$ of thickness and $1.95 \pm 1.5\%$ of gauge factor. The *element* 5 is a polyurethane paint called PU 120 which acts as a covering agent for the SG. It protects the gauge from the external effects such as humidity or mechanical damage. It ensures equal resistance of the gauge from oils, alcohols and certain acids, thus, making the present system to work under harsh conditions too.

3.2. Experimental setup for wear and particle aerosol measurement

Fig. 3 shows the complete experimental set-up for carrying out the abrasion wear tests as well as the in-process aerosolization analysis of the wear particles. Particle free air is passed through a work post containing the modified Taber abrasion apparatus. Keeping the motor outside, its linearly sliding part is kept inside an *emission test chamber* (Le Bihan et al., 2014a). This allows for avoiding any influence of the abrasion apparatus' motor emissions to the test result. This possibility is a further feature of the Taber set-up, which cannot be easily achieved for any tribometer. The emission test chamber finds its use in other particle aerosolization tests too (Morgeneyer et al., 2013; Le Bihan et al., 2014b). The particle aerosols getting generated during the abrasion wear are analyzed using a Condensation Particle Counter (CPC; Model 3775; TSI Inc., USA; measurable size range: 4 nm to $3\ \mu\text{m}$), an Aerodynamic Particle Sizer (APS; Model 3321; TSI Inc., USA; measurable size range: 0.5– $20\ \mu\text{m}$), a Scanning Mobility Particle Sizer (SMPS; Model DMA 3081 and CPC 3775; TSI Inc., USA; measurable size range:

15–600 nm) and a Mini Particle Sampler (MPS®; Ecomasure Inc., France) (R'mili et al., 2013). A MPS is used for the particle collection through filtration technique on porous grids which can be used later in transmission electron microscopy (TEM) for various qualitative analyses of the released particles.

The operation conditions of these instruments are as follows: CPC – flow rate of 1.5 l/min with 1 s of sampling time; SMPS – flow rate of 0.3 l/min with 120 s of sampling time; APS – flow rate of 5 l/min with 5 s of sampling time). A proper measurement of F_T is ensured through a dynamic SG amplifier (Model EspressoDAQ DQ 430; HBM GmbH, Germany) which is connected in series to the SG, thus allowing a reliable measurement of the strain produced in the gauge. The data transmitted via amplifier is acquired using CATMAN® software (Model Starter; HBM GmbH, Germany).

3.3. Calibration of the strain gauge

Two simple and reliable traction tests have been employed for the calibration of the present modification. As illustrated in Fig. 4, the traction test I involves the load application via pulley and keeping the apparatus horizontally (i.e. in its usual position) while the test II involves a direct load application (i.e. without a pulley) with a vertically held Taber apparatus. These tests ensure the calibration of the SG in the same conditions in which it is used in reality. The SG was set with an acting voltage of 1 V, data acquisition frequency of 500 Hz, ambient temperature conditions and relative humidity at 60% (approx.). Based on an extensive literature survey (Boentoro et al., 2009; Sepeur et al., 1999; Katsamberis et al., 1998; Wank et al., 2006; Huang and Tseng, 2000) (not all the references consulted are provided here) on the experimental conditions in which the standard apparatus has been used, the suspended load has been chosen to vary from 0 to 20 N with the incremental steps of 0.5 N. In Fig. 5, the SG signal corresponding to the gradually increasing suspended load is shown in two test conditions. Two linear curves, superimposing each other, can be seen in the figure which shows the reliance of the obtained data in the applied load range.

It is worth to note that in the test conditions I and II, the SG equipped bar was tested while remained fixed in the Taber apparatus through a series of screws (same way of fixing as in the original Taber apparatus). Such loading conditions introduce deformations to the bar even without applying any further external load. This is the reason of having negative signal value under zero applied load. This was further verified by another test (test III, not shown in Figs. 4 and 5) which consists of unscrewing the SG equipped bar from the apparatus

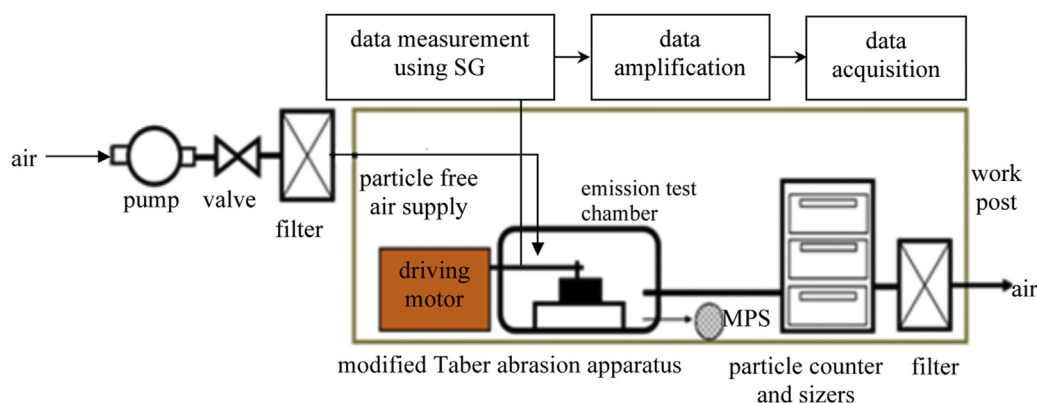


Fig. 3 – Experimental set-up.

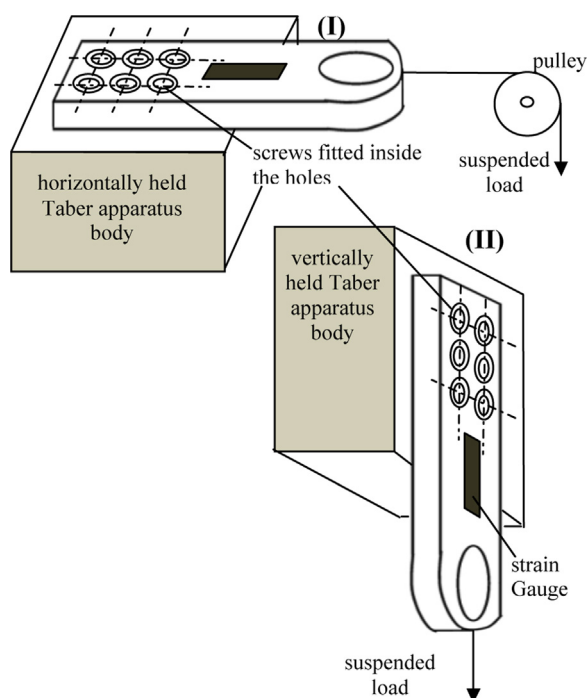


Fig. 4 – Experimental setup for calibration tests: I – suspended load connected to the horizontally held SG equipped aluminum bar via pulley and II – suspended load connected to the vertically held SG equipped aluminum bar.

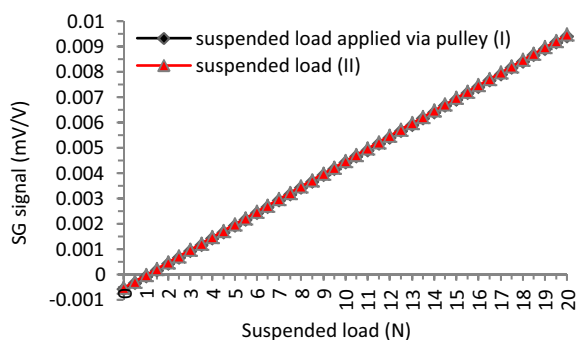


Fig. 5 – Response of the SG to the applied load under three different load conditions.

and subjecting it to a tensile test through a Universal Tensile Testing Machine (UTM). As expected, the SG showed zero value under no applied load. However, the data from test III have not been taken into account in Fig. 5 because the stresses involved in this test do not represent the same stresses as to which the

bar is subjected in reality. Based on the data shown in Fig. 5, a mean curve can be deduced which calibrates the SG signal, V (in mV/V) in terms of F_T (in N) using an empirical relation:

$$F_T = 2000V + 1.14 \quad (3)$$

For this mean curve, the minimum and maximum standard deviation in the SG signal values are 3.05×10^{-5} mV/V and 3.7×10^{-4} mV/V, respectively.

3.4. Validation of the modification

To validate the modification made in the Taber apparatus, abrasion tests were performed on a masonry brick – one using the modified apparatus and the other using a commercial linear tribometer (Model TE77; Plint Inc., UK) which fulfills the ASTM G133 and ASTM G115 standards (ASTM, 2010a, 2010b). The test conditions were similar for both tests i.e. constant abrasion speed of 60 cycles/min, Taber H38 non-resilient vitrified clay-carborundum abraser and constant $F_N = 8$ N (set by putting a dead load for the Taber apparatus whereas controlling spring lever system for the Plint tribometer). The results for 10 abrasion cycles were compared. One cycle has been shown in Fig. 6(a) with clear static (e.g. 0–0.06 s) and dynamic (e.g. 0.06–0.5 s) friction ranges. The comparison of the tangential force values in the dynamic friction range for all 10 cycles has been done using a frequency distribution in Fig. 6(b). From the figure, the negative regime (i.e. the back movement) seems to have a steeper frequency distribution than the positive one (i.e. the forth movement) for both instruments. Also, the measured value of F_T is underestimated by the modified Taber abrasion apparatus (4.3 N against 4.5 N from Plint TE77 in negative regime and 4.2 N against 4.6 N from Plint TE77 in positive regime). Therefore, the offset error (ΔF_T) is 0.2 N in negative and 0.4 N in positive regime with respect to Plint TE77. If $\bar{F}_T$ is the final value obtained by averaging all the absolute values of F_T from modified Taber apparatus in positive and negative regimes during dynamic friction range and taking the value of F_T measured by Plint TE77 as reference, then $\bar{F}_T = 4.2 \pm 0.3$ N.

4. Preliminary case studies

The present modified apparatus has been employed in numerous case studies related to the tangential force measurement having various material–abraser couples. Out of them, three are presented here – an alumino-silicate masonry brick with Taber H38 abraser, a plywood board with Taber H38 abraser

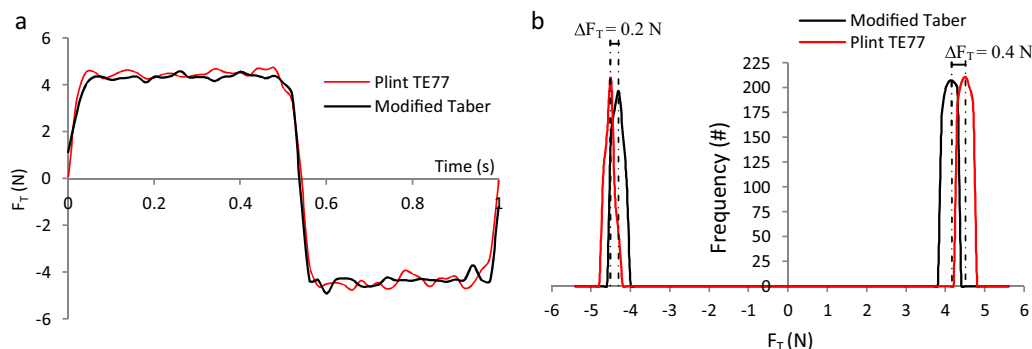


Fig. 6 – (a) Comparison of tangential forces measured using Plint TE77 tribometer and modified Taber abrasion apparatus under same experimental conditions. (b) Frequency distribution of the data on tangential force measured using Plint TE77 and modified Taber abrasion apparatus in the dynamic friction range during 10 cycles.

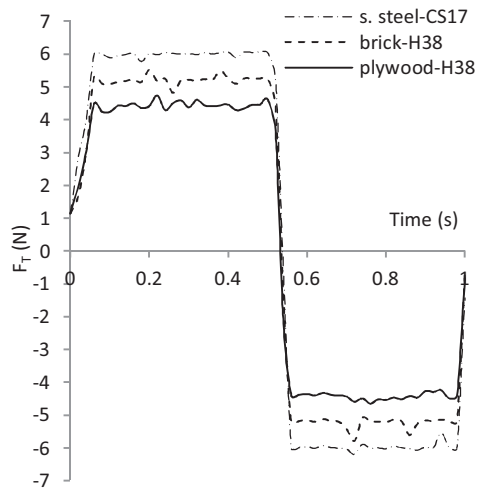


Fig. 7 – Tangential force measurement for the three material-abraser couples.

and a stainless steel sheet with Taber CS17 resilient rubber-alumina abraser. The abrasion speed has been kept constant at 60 cycles/min with the same and constant normal force $F_N = 9\text{ N}$ for all tests. The tests were repeated three times for each material and each test consisted of 10 abrasion cycles. The resulting mean curves are shown in Fig. 7(a) (std. deviation = 0.117 N for brick; 0.112 N for stainless steel; and 0.161 N for plywood). With clearly visible static (0–0.05 s) and dynamic friction ranges (0.05–0.5 s) in each stroke, three distinct curves for three different materials can be observed. The $\bar{F}_T$ is equal to $5.98 \pm 0.3\text{ N}$ for stainless steel-CS17 couple; $5.22 \pm 0.3\text{ N}$ for brick-H38 couple; $4.43 \pm 0.3\text{ N}$ plywood-H38 for couple.

As mentioned earlier and shown by (Jiang et al., 1998), E_W is a direct function of the material removal mechanism and since E_W depends on F_T , therefore, F_T should also be a direct function of the material removal mechanism. Further to Archard's approach (Eq. (1)), no – possibly linear – friction relationship between F_N and F_T needs to be hypothesized in this case. In order to primarily observe the mechanism, the worn surfaces were analyzed using a Surface Profilometer (Model 400; Precision Devices Inc., USA) and a Scanning Electron Microscope (QUANTA ESEM™ 400; FEI Inc., The Netherlands). Fig. 8 shows the results: in Fig. 8(a), the results for the worn brick surface are shown. A rough worn surface with rms value = $15.8\text{ }\mu\text{m}$ and brick's brittle nature suggest the brittle fracture of the surface asperities whereas in the case of stainless steel (Fig. 8(b)), being a ductile material, it appears to undergo abrasive wear via plastic deformation. The SEM image shows the development of the grooves on the surface which can get created by the displacement of the material to sideways of the abrasive grains during abrasion, i.e. *ploughing*. The rms value of the roughness measured in this case is $10.3\text{ }\mu\text{m}$.

In Table 1, the total particle number concentration (i.e. total number of particles having size in the range of 4 nm to $3\text{ }\mu\text{m}$

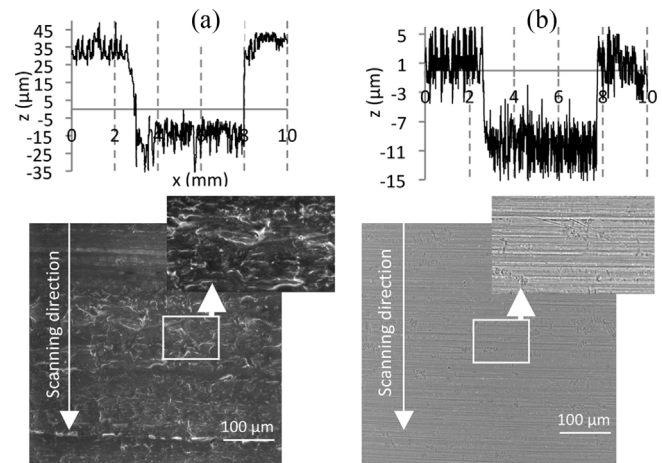


Fig. 8 – Surface profiles and their microscopic images of worn (a) brick and (b) stainless steel test samples.

present in 1 cm^3 of air, TPNC) and size mode (i.e. the particle size interval having the highest concentration) in the particle size distribution of the aerosolized particles during abrasion for the three substrate-abraser couples are shown with their $\bar{F}_T$ values. While TPNC can be measured directly from the CPC 3775, the size modes are measured using the SMPS 3081 and APS 3321. With the highest value of $\bar{F}_T = 5.98 \pm 0.3\text{ N}$ during assumed plastic deformation for the stainless steel-CS17 couple, both TPNC and size mode hold the minimum values, i.e. 108 cm^{-3} and 75 nm , respectively. In case of material removal mechanisms like probably fracturing or cutting (as in brick and plywood), $\bar{F}_T$ holds relatively lower values but higher TPNC and size mode values. Clearly, like $\bar{F}_T$, both TPNC and size mode also appear to be the function of the material removal mechanisms during wear. This correlation needs to be further investigated in order to assess the predictability of the aerosolization of wear particles when the wear conditions are known.

5. Conclusion and outlook

In the present work, it has been shown that a standard Taber abrasion apparatus can be equipped with a strain gauge to know the complete stress state during abrasion wear and be coupled with particle sizers and counters to determine the concentration of the resulting aerosolized wear particles at the same time. This represents a significant improvement for the standard Taber abrasion apparatus which finds its use limited presently when the complete stress state or wear energy needs to be known. The data gathered from this apparatus has been found to be reliable given the linearity found in calibration (Fig. 5) and a behavior close to that of a commercial tribometer (Fig. 6(a) and (b)). $\bar{F}_T$, TPNC and size mode of the aerosolized particles concentration appear to be the function of the material removal mechanism during wear.

Table 1 – Comparison of the number concentrations and size modes of the released particles to corresponding $\bar{F}_T$ for the three material substrate-abraser couples.

Material substrate	Abraser type	$\bar{F}_T$ (N)	Total particle number concentration (cm^{-3})	Size mode (nm)
Stainless steel	CS17	5.98 ± 0.3	108	75
Brick	H38	5.22 ± 0.3	653	237
Plywood	H38	4.43 ± 0.3	742	523

The modification presented in the article is thus a set-up for the simultaneous quantitative study of both wear and its in-process aerosolization. Further improvements of the work post are due in future which would take into account and minimize the losses (if any) in the concentration of the particle aerosols due to their deposition on the surfaces of the worn material, emission chamber and the aerosol conducts, thus enabling for a fully quantitative investigation of the aerosolization of particles by wear. Furthermore, investigation of the aerosolized debris, sampled by means of an MPS, will be carried out. Here, particularly for (nano-) coated structures, the analysis of the debris particles with respect to their composition will be of particular interest (Shandilya et al., 2014c).

References

- ASTM International, 1996. *Standard Test Methods for Dry Abrasion Wear Resistance of High Gloss Coatings*, ASTM D6037.
- ASTM International, 2007. *Standard Test Method for the Abrasion of Organic Coatings by the Taber Abraser*, ASTM D4060.
- ASTM International, 2008. *Standard Test Method for Resistance of Transparent Plastics to Surface Abrasion*, ASTM D1044.
- ASTM International, 2010a. *Standard Test Method for Linearly Reciprocating Ball-on-Flat Sliding Wear*, ASTM G133-05.
- ASTM International, 2010b. *Standard Guide for Measuring and Reporting Friction Coefficients*, ASTM G115.
- Boentoro, W., Pflug, A., Szyzyska, B., 2009. Scratch resistance analysis of coatings on glass and polycarbonate. *Thin Solid Films* 517, 3121–3125.
- Fouvry, S., Liskiewicz, T., Kapsa, Ph., Hannel, S., Sauger, E., 2003. An energy description of wear mechanisms and its applications to oscillating sliding contacts. *Wear* 255, 287–298.
- Gohler, D., Stintz, M., Hillemann, L., Vorbau, M., 2010. Characterization of nanoparticle release from surface coatings by the simulation of a sanding process. *Ann. Occup. Hyg.* 54 (6), 615–624.
- Golanski, L., Guiot, A., Pras, M., Malarde, M., Tardif, F., 2012. Release-ability of nano fillers from different nanomaterials (toward the acceptability of nanoproduct). *J. Nanopart. Res.* 14, 962–970.
- Hegadekatte, V., Kurzenhauser, S., Huber, N., Kraft, O., 2008. A predictive modeling scheme for wear in tribometers. *Tribol. Int.* 41, 1020–1031.
- Hokkirigawa, K., Kato, K., 1988. An experimental and theoretical investigation of ploughing, cutting and wedge formation during abrasive wear. *Tribol. Int.* 21, 51–57.
- Huang, C.-Y., Tseng, C.-I., 2000. The effect of interface modification between POM and PTFE on the properties of POM/PTFE composites. *J. Appl. Polym. Sci.* 78, 800–807.
- Jiang, J., Sheng, F., Ren, F., 1998. Modelling of two-body abrasive wear under multiple contact conditions. *Wear* 217, 35–45.
- Katsamberis, D., Browall, K., Iacovangelo, C., Neumann, M., Morgner, H., 1998. Highly durable coatings for automotive polycarbonate glazing. *Prog. Org. Coat.* 34, 130–134.
- Le Bihan, O., Shandilya, N., Gheerardyn, L., Guillon, O., Dore, E., Morgeneyer, M., 2013. Investigation of the release of particles from a nanocoated product. *Adv. Nanopart.* 2, 39–44, <http://dx.doi.org/10.4236/anp.2013.21008>.
- Le Bihan, O., Morgeneyer, M., Shandilya, N., Chariol, O.A., Bressot, C., 2014a. Emission chambers, a method for nanosafety, 01/2014. In: Vogel, U., Savolainen, K., Wu, Q., van Tongeren, M., Brouwer, D., Berges, M. (Eds.), *Handbook of Nanosafety – Measurement, Exposure, Toxicology*. AP/Elsevier, San Diego, pp. 226–231, ISBN: 9780123456789 (Chapter 7.2).
- Le Bihan, O.L.C., Ustache, A., Bernard, D., Aguerre-Charriol, O., Morgeneyer, M., 2014b. Experimental study of the aerosolization from a carbon nanotube bulk by a vortex shaker. *J. Nanomater.* 2014, <http://dx.doi.org/10.1155/2014/193154>, Article ID 193154 (in press).
- Meng, H.C., Ludema, K.C., 1995. Wear models and predictive equations: their form and content. *Wear* 181–183, 443–457.
- Morgeneyer, M., Le Bihan, O., Ustache, A., Aguerre-Charriol, O., 2013. Experimental study of the aerosolization of fine alumina particles from bulk by a vortex shaker. *Powder Technol.* 246, 583–589.
- R'mili, B., Le Bihan, O., Dutouquet, C., Aguerre-Charriol, O., Frejafon, E., 2013. Particle sampling by TEM grid filtration. *Aerosol Sci. Technol.* 47, 767–775.
- Riester, M., Lutz, A., Hilgers, H., Friedrich, K., 1997. Taber abraser/liquid particle count coupling for the determination of sliding wear of metallized plastics. *Surf. Coat. Technol.* 97, 649–655.
- Rossi, S., Deflorian, F., Risatti, M., 2006. Modified Taber apparatus and new test geometry to evaluate the reduction of organic coatings corrosion protective properties induced by abrasive particles. *Surf. Coat. Technol.* 201, 1173–1179.
- Schlagenhauf, L., Chu, B.T.T., Buha, J., Nüesch, F., Wan, J., 2012. Release of carbon nanotubes from an epoxy-based nanocomposite during an abrasion process. *Environ. Sci. Technol.* 46, 7366–7372.
- Sepeur, S., Kunze, N., Werner, B., Schmidt, H., 1999. UV curable hard coatings on plastics. *Thin Solid Films* 351, 216–219.
- Shandilya, N., Le Bihan, O., Bressot, C., Morgeneyer, M., 2013. Wear characterization towards the study of particle emission tendency. In: *World Tribology Congress*, Turin, Italy, ISBN 978-88-90818509.
- Shandilya, N., Le Bihan, O., Morgeneyer, M., 2014a. A review on the study of the generation of (nano) particles aerosols during the mechanical solicitation of materials. *J. Nanomater.* 2014, <http://dx.doi.org/10.1155/2014/289108>, Article ID 289108, 16 pp.
- Shandilya, N., Le Bihan, O., Morgeneyer, M., 2014b. Effect of the normal load on the release of aerosol wear particles during abrasion. *Tribol. Lett.*, <http://dx.doi.org/10.1007/s11249-014-0351-y>.
- Shandilya, N., Le Bihan, O., Bressot, C., Morgeneyer, M., 2014c. Evaluation of the particle aerosolization from n-TiO₂ photocatalytic nanocoatings under abrasion. *J. Nanomater.* 2014, <http://dx.doi.org/10.1155/2014/185080>, Article ID 185080, 11 pages.
- Vorbau, M., Hillemann, L., Stintz, M., 2009. Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings. *Aerosol Sci.* 40, 209–217.
- Wank, A., Wielage, B., Pokhmurska, H., Friesen, E., Reisel, G., 2006. Comparison of hardmetal and hard chromium coatings under different tribological conditions. *Surf. Coat. Technol.* 201, 1975–1980.

7.2 EMISSION CHAMBERS, A METHOD FOR NANOSAFETY (LE BIHAN, MORGENEYER, SHANDILYA, AGUERRE, BRESSOT)

7.2.1 Introduction

Determining the risk of exposure to nanomaterial inhalation at a workstation is a complex process. Many questions beg for answers, in particular concerning the source of the particles. What precisely is the source? Are there multiple sources? How do you distinguish the sources and measure background noise? How does the source work, and in particular, when and for what reasons does this source start emitting particles? What are the physical and chemical properties of the particles? What kinds of quantities are emitted?

In view of answering such questions, industrial hygiene researchers and engineers require further information and data. Measures may be taken on site, and studies carried out in the lab. For the latter, the emission chamber is a high-performance tool that may be used under specific conditions.

7.2.2 Presentation of the Concept

International standards [6,7] define emission chambers as a test method dedicated to measuring the discharge of volatile organic compounds (VOC) in indoor air. In the absence of a specific standard pertaining to the release of (nano-) particles, it becomes possible to use such documents as a starting point.

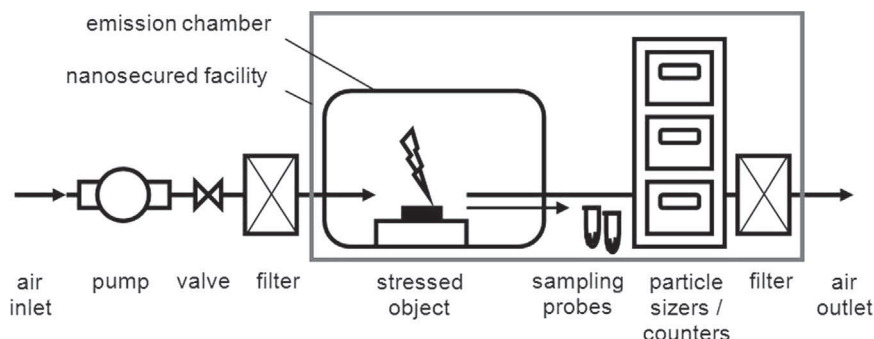


FIGURE 7.1 Schematic diagram of an emission chamber.

7.2.2.1 Description and Operation

The operating principle of an emission chamber is very simple (see Figure 7.1). Air from a clean source is conducted through a conduit to the chamber, which is sealed. The sample brought to this enclosed space is then stressed in various ways (using mechanical abrasion, etc.). The air, potentially loaded with particles, is then evacuated through a conduit leading on the one hand to on-line particle counters (for the detection of particles during the test) and on the other hand to particle extraction systems enabling a series of off-line analyses of particle composition using transmission or scanning electronic microscopy (SEM, TEM). The complete installation may be placed under a hood to guarantee confinement (nanosafety).

The goal is to create testing conditions that are similar to real conditions and to document them. Standards in relation to VOCs [6,7] establish specifications in terms of temperature and relative air humidity, as well as airflow and air velocity rates (0.1 m/s to 0.3 m/s). System leaks should not exceed 0.5% of the chamber volume per minute when over-pressurized at 1 kPa.

7.2.2.2 Definitions and Physical Principles

The main definitions supplied for the case of VOCs [6,7] are summarized below and are applicable to the study of airborne particles. *Background noise* is defined as the quantity of particles present in the chamber independent of the source under study. It is linked to the quality of the clean air injected into the chamber, and to additional sources. The lower the background noise, the lower the detection threshold for measurements.

The emission phenomenon may be observed through time depending on the *clean air exchange rate* of the chamber (flow rate of clean air to the chamber divided by its air volume (1/h)). *Specific air flow* (e.g., per sample

surface under study ($(\text{m}^3/\text{h})/\text{m}^2$) is a fundamental unit which enables comparison of *emission rates* across various studies, that is, the mass of particles emitted per unit time (mg/h). The *specific emission rate* q (also referred to as *emission factor*) may be defined relative to the dictates of the study – per unit q_U (e.g., the number of objects introduced into the chamber, $(\text{mg}/\text{h}/1)$), length q_L (e.g., long objects $(\text{mg}/\text{h}/\text{m})$), surface q_S (default scenario, if release of particles from surfaces is under study $(\text{mg}/\text{h}/\text{m}^2)$), volume q_V ($\text{mg}/\text{h}/\text{m}^3$) and mass q_M ($\text{mg}/\text{h}/\text{kg}$).

A simple time-dependent mass balance may be defined assuming a ‘uniform’ flow rate: $V \frac{dC(t)}{dt} = R(t) - QC(t) - S(t)$, where V is the volume of air present in the chamber (m^3), $C(t)$ is the mass of particles evacuated with the loaded air (mg/m^3), $R(t)$ is the rate of release from the object to the chamber (mg/h), Q is the clean air flow rate feeding into the emission chamber (m^3/h), $S(t)$ are stray particles on the walls of the chamber, conduits or the object itself (mg/h), and t is time measured in hours, for example, starting when the object is introduced into the emission chamber.

Stray particles S may be limited with an appropriate layout of the air inlet and of air sampling in the chamber, for example, directly at the level of an abrasion site.

7.2.3 Case of Intentional and Non-Intentional Particles

Studies dedicated to ultrafine particles (non-intentional particles with a diameter less than 100 nm) in indoor air [8] used a large volume emission chamber (e.g., 70 m^3 [57], 32 m^3 [9]) or a smaller volume (e.g., 2.5 m^3 [10]). Except for Koponen et al. (20.6 m^3 [11]), studies dedicated to nanomaterials all used chambers with smaller volumes. Vorbau et al. [12] worked with a 1.5 L volume, and INERIS used 80 L to 500 L chambers [13,14]. All of the studies were conducted with a filtered air inlet, with varying self-defined requirements concerning background noise (e.g., $< 20 \text{ p}/\text{cm}^3$ [15]).

A minority of authors precisely qualify experimental conditions (air exchange rate, etc.), evaluating and factoring in stray particles on the walls and sampling lines (e.g., [10]). There are to date only a few researchers who express their findings in terms of ‘emission factors’ and who supply repeatability data (i.e., consolidation of their findings with repeated testing under same conditions), although this is one of the advantages of emission chambers (e.g., Figure 7.2d).

In the majority of cases, the authors sought to characterize and quantify the particles emitted from the materials-stress couple under consideration. The point is also to determine whether the nanoloads used with materials are yielding individual free nanoparticles, or heterogeneous matrix-nanomaterials (e.g., polymers).

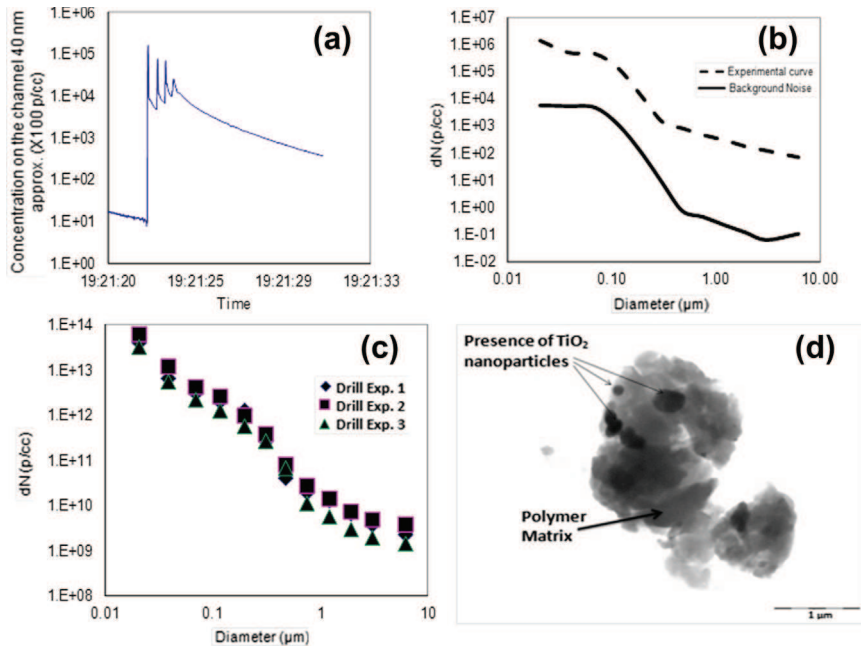


FIGURE 7.2 (a) Time-based monitoring during four successive grinding tests; (b) medium-size distribution during pumicing in comparison to background noise; (c) number of particles emitted during drilling — three tests; (d) example of a heterogeneous particle consisting of the (polymer) matrix and TiO₂ nano-charge.

The stress tests under study were varied [13]: pumicing [13,14,16], UV radiation and friction combined [15], abrasion [12,17], sanding [11], piercing [14].

In the majority of cases, real-time measurement tools are used: particle counters (CPC) measuring total number concentration for sizes ranging from a few nanometers to a micron; spectrometers for measuring particle number size distributions from a few nanometers to a micron (SMPS, FMPS, DMS) and beyond (ELPI); optical counters (OPC) measuring particle sizes from around 0.3 μm up to 15–20 μm.

This real-time measure makes it possible to determine background noise in the emission chamber and to observe the impact of the events triggered by the scientist.

It should be noted that mechanical units used for the application of stresses to a material in an emission chamber can also considerably influence and hence contaminate the particle concentration in the chamber. They themselves act as a potential source of particle emission, for example, motor brush, rotors, etc. The ideal solution to avoid such a situation is to place these units outside of the chamber (e.g., in [13]).

In the example presented in Figure 7.2a–c, the scientist performed a series of four pumicing tests in succession on a nanostructured object. Impact within the emission chamber is clearly observable (Figure 7.2a), since as a result of these operations, the total concentration of the chamber changes from $10^3/\text{cm}^3$ (background noise) to $10^6\text{--}10^7/\text{cm}^3$. Particles emitted, in the present case, concern the totality of the size spectrum (Figure 7.2b). Knowing the initial background noise makes it possible to calculate the impact of the source.

Sampling for a microscopic analysis is used in more than half of the studies, and is conducted mainly via electrostatic precipitation.

This approach will likely become systematic. It is facilitated by an easy and new technique, the filtration by porous TEM grid (e.g., by MPS® [18]). Indeed, it enables the study of nanocharge, and in particular whether they remain within the matrix as heterogeneous particles (see Figure 7.2d), or whether they are released as free particles.

7.2.4 Discussion

Because of the controlled atmosphere that is afforded, an emission chamber makes it possible to focus on a single source, i.e., to ignore background noise in the atmosphere and from other sources. A very large range of measuring materials for aerosols may be used as this is laboratory testing. In particular this makes it possible to use devices that are otherwise difficult to use in the field (e.g., SMPS). Consequently, the physical and chemical characterization of the aerosol is very comprehensive.

An emission chamber is a small device that is relatively easy to use, which facilitates the carrying out of tests. The installation can easily be changed and modified.

However, this approach may only be adopted in a situation that can be modelled on an experimental basis. This actually sets the limit, for example, for complex and/or voluminous processes.

7.2.5 Conclusion and Future Prospects

Despite a limited number of references, it is already possible to conclude positively as regards the usefulness of an emission chamber for the study of NM emissions.

To date, use of this device remains new and ‘exploratory’. The device’s potential is still not fully utilized. This holds true for the determination of ‘emission rates’, which enables the modelling of particle dispersion and the study of exposure scenarios.

Harmonization of practices via standardization would facilitate the comparison of studies and promote the development of tests recognized by all members of the professional community, or even at a regulatory level.

Acknowledgements

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5. EXPERIMENTAL RESULTS OF EMISSION FROM NANOSTRUCTURED PRODUCTS: CASE STUDIES

As mentioned earlier in the introduction section, ENM are used in a wide range of applications and have become part of everyday life. With their increased use, concerns have been raised about their potential negative impacts on human health and the environment. In view of a sustainable development of nanotechnologies, possible risks have to be investigated and communicated. A risk posed by ENM may only arise if exposure and a hazard potential coexist. Hazard potential may be expressed as the material's human or eco-toxicity.

The focus of this section is on the release and consequently the potential exposure to ENM during the phase of its use by a consumer. So far, too little is known about the different release processes such that only very specific case studies can be conducted. Therefore, three case studies are presented here which talk about the ENM release from two different nanostructured products: Masonry brick reinforced with TiO_2 nanoparticles and Photocatalytic nanocoatings containing TiO_2 nanoparticles respectively. Whilst in the first two case studies the effect of the mechanical stresses on the release tendency of TiO_2 is investigated from these two products, in the third case study, the mechanical stresses further couples with environmental weathering. The TiO_2 nanoparticles are considered here because they are one of the widely used ENM in the commercial nanostructured products. Their presence in a product not only ensures better mechanical properties and longer lives but also imparts some photocatalytic effects too which includes properties like self-cleaning, air purifying, antibacterial and super hydrophilic.

5.1 Emission from reinforced brick

In this first case study, TiO_2 nanoparticles reinforced masonry brick is tested for its ENM emission tendency during abrasion. These types of bricks are readily being used in our daily lives during the construction of the house walls, pavements, façades etc. As a result, they are a potential target of the mechanical stresses which might act on them from day to day.

To show various details on abrasion tests and their results, an article, entitled "Effect of the normal load on the release of aerosol wear particles during abrasion" is provided. In this article, the abrasion of a brick, containing nanoparticles of TiO_2 in its bulk, is carried out using an abrasant Taber H38. This abrasant is in a 2 cm long and 6 mm wide cylindrical form with abrasive grains of carborundum embedded inside a matrix of clay. Another purpose served by this article is that it elucidates the role of the normal force as one of the important key parameters in the ENM emission, as said in the section 3. The size of the emitted aerosol particles is shown to increase with the increase in normal force. The number concentration which was observed to increase initially with the normal force starts decreasing as soon as an intermediate value of the normal force (i.e. $F_N \approx 10.5$ N in this case) is reached for the particle size range of 20 to 500 nm. However, for the size range 0.5 to 20 μm , it remained constant. In the case of the mean size of the emitting aerosol particles, a monotonous increase was observed. Furthermore, a conceptual model is also presented in this article which illustrates the process of the material removal during abrasion of this particular brick which ultimately yields the ENM emission. This model does not consider the role of thermo-mechanical stresses as a result of frictional heating of the contact. It also excludes the role of three body abrasive wear of the brick surface during ENM emission. In such a type of wear, a fraction of the generated wear debris particles gets entrapped between the surfaces of the abrasant and brick. They then roll and slide there which contributes in the generation of more wear debris particles.

Effect of the Normal Load on the Release of Aerosol Wear Particles During Abrasion

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Abstract A study highlighting the aspect of the generation of aerosol wear particles during abrasion is presented. The substrate chosen is a masonry brick which is reinforced with TiO₂ nanoparticles. This is done using a pin on plate arrangement. The material removal mechanism via fracturing is first understood. The parameter chosen for the study is the normal load. The formed aerosols are then characterized by their number concentration, particle size distribution, individual particle shape, size and chemical composition. Having irregular shapes, the aerosol wear particles have unimodal size distributions with 5–7 % (in mass) of Ti content. The size mode increases with the increase in normal load. However, at higher normal loads, while there is an unexpected increase in the wear mass, the maximum concentration of the aerosol particles saturates. During the whole study, no free nanoparticles of TiO₂ were found.

Keywords Aerosol · Wear · Abrasion · Nanoparticle · Fracturing · Size distribution

List of symbols

C_c Slip correction factor
 d Inside diameter of the tube
 d_i Large diameter
 d_o Small diameter

d_p Particle diameter
 D Diffusion constant of the particles
 g Gravitational acceleration
 L Length of the tube
 P Absolute pressure
 Q Volume flow rate through tube
 Re Reynolds number
 Stk Stokes number
 U Sampling velocity
 $\bar{U}$ Average flow velocity in the tube
 V_{dep} Diffusive deposition velocity
 V_t Deposition velocity for turbulent inertial deposition
 V_{ts} Particles settling velocity
 ρ_g Gas density
 ρ_p Particle density
 θ Angle of inclination of the tube from horizontal
 η Gas viscosity
 φ Angle of bend in radians
 τ Particle relaxation time
 Θ Contraction angle

1 Introduction

The improvement of the construction material properties has always been an important research topic in the industries. These construction materials can be used in the houses, roads, buildings etc. Some of these construction materials are frequently reinforced with the nanoparticles of titanium dioxide (TiO₂). Such a nanotreatment not only ensures better mechanical properties [1–3] but also imparts some photocatalytic effects too in the material [4–6] which includes self-cleaning, air purifying, antibacterial, odor destructive, super hydrophilic and antistatic

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Table 1 Material properties of the brick

Property	Value
Composition	Al, Si, Ca, Ti
RMS roughness	7 μm
Average primary particle size of TiO_2	<20 nm
Elastic modulus	20 GPa
Poisson's ratio	0.2
Vickers hardness	~800

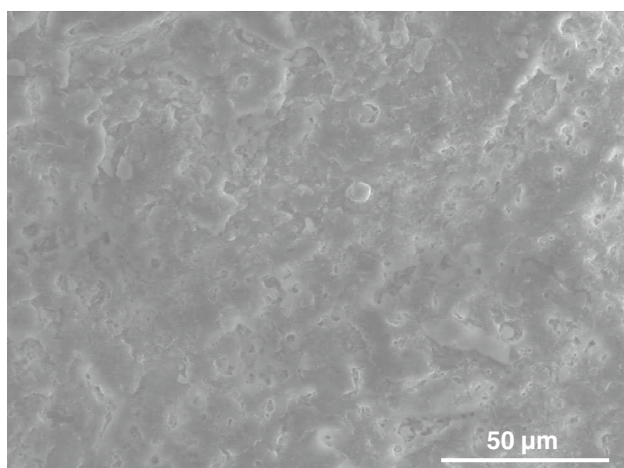


Fig. 1 SEM image of the masonry brick

properties. However, during their lifecycle, these nanoparticles-reinforced materials are subjected to various mechanical stresses in the form of their handling, use or processing [7–9]. This may result in their eventual surface wear and the aerosol particles containing TiO_2 nanoparticles may start to get released in air [10–12]. Upon exposure, these released TiO_2 nanoparticles may interact with the human organism through inhalation or dermal contacts and get deposited inside the body. Various toxicological studies have demonstrated toxic effects of some types of TiO_2 nanoparticles in this case [13–15]. Few studies have examined the concentration, morphology and chemical composition of the generated aerosol wear particles [16–18]. In spite of this, there is no sufficient contextual information in the literature [9]. To better understand this, the aerosol release evaluation during material wear is very critical.

The study presented here aims to evaluate aerosol particle release or aerosolization from a commercially available masonry brick which is reinforced with TiO_2 nanoparticles. For simulating the stress conditions to which such bricks are subjected to, their abrasion is done. The parameter chosen for the study is the normal load acting

during abrasion. An experimental setup is developed where the aerosol particles, after getting generated from abrasion, are characterized by aerosol measurement devices both in quantitative as well as qualitative ways.

2 Materials and Methods

2.1 Substrate

A masonry brick, reinforced with TiO_2 nanoparticles, (11 cm $\times$ 5 cm $\times$ 5 cm; Leopard brick, Ref: 901796, Castorama) was used for the study as a substrate. It is basically an alumino-silicate brick which is frequently used in constructing façades, house walls, wall tiles, pavements etc. Its material properties along with a scanning electron microscope image (QUANTA ESEMTM 400, FEI Inc. The Netherlands) are shown in Table 1 and Fig. 1, respectively.

2.2 Abrasion Process

The standard Taber linear abrasion apparatus (Model 5750; Taber Inc. USA) was used for the abrasion of the brick. The apparatus is referenced in numerous internationally recognized test standards [19–21]. It incorporates a motor-driven horizontal arm/bar that displaces an abrasant in a back and forth linear motion over the test sample. The abrasion is caused by the friction at the contact surface between the surfaces of the abrasant and the sample. Via a vertical shaft, a known weight is mounted on the top of the abrasant which shall be referred as the Normal Load (F_N) in the text. The abrasiveness can be varied by changing the type of the abrasant and normal load value. It is imperative to apply a reproducible and standardized stress on the test samples for reproducible tests. This has been ensured through preliminary tests and contextual literature survey on the optimal adjustment of the Taber abrasion apparatus [22–26].

2.3 Parameters Studied

The effect of the normal load (i.e., 6, 7.5, 9, 10.5, 12, 13 and 14 N) on the number concentration of released aerosol particles was studied. The details on other experimental conditions are provided in Table 2. A Taber H38 non-resilient vitrified clay-carborundum abrasant was used during the whole study [27]. With a standard 6-mm-diameter cylindrical shape and Vickers hardness of $\sim 3,100 \text{ kg/mm}^2$, this abrasant comprises of very fine abrasive particles of carborundum (shown in Fig. 2) that provide mild abrasion.

Table 2 Experimental parameters (repetition of the tests: 3 times)

Test sample	Abrasion speed (cycles per minute or cpm)	Normal load							Abradant	Stroke length (mm)	Number of cycles
		6 N	7.5 N	9 N	10.5 N	12 N	13 N	14 N			
Masonry brick	60	X	X	X	X	X	X	X	H38	76	600

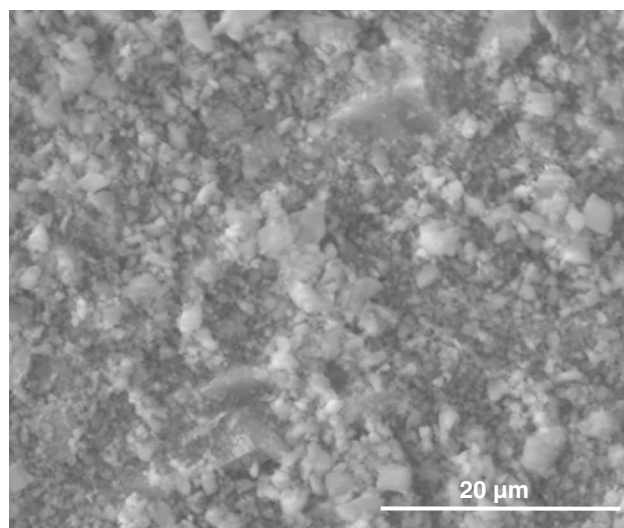


Fig. 2 SEM image of the Taber H38 abradant

2.4 Experimental Setup

Figure 3 shows the scheme of the complete experimental setup. Particle free air is passed through a nanosecured work post (HPPE 10, Erma Flux S.A., France) [28, 29] containing the Taber abrasion apparatus. This work post has a particle filter efficiency of $\sim 99.99\%$. The test sample is placed inside a self designed Emission Test Chamber ($0.5\text{ m} \times 0.3\text{ m} \times 0.6\text{ m}$) [30]. A slot is provided on one of the walls of this chamber allowing the horizontal arm of abrasion apparatus passing through and operating the apparatus (equipped with motor) to be placed externally. The sampling of the generated aerosol particles is done in a close proximity (10 cm) of the test sample. The Taber apparatus along with the emission test chamber constitutes aerosol generation section. The aerosol particles, getting generated during the abrasion process, are characterized in terms of their number concentration and number size distribution. Using anti-static electrically conductive tubes (6 mm diameter), the aerosol generation section is combined with an aerosol measurement section. The aerosol measurement section consists of a Condensation Particle Counter (CPC; Model 3775; TSI Inc. USA; measurable size range 4 nm – $3\text{ }\mu\text{m}$), a scanning mobility particle sizer (SMPS: Model DMA 3081 and CPC 3775; TSI Inc. USA; measurable size range 15 – 500 nm), an

Aerodynamic Particle Sizer (APS; Model 3321; TSI Inc. USA; measurable size range 0.5 – $20\text{ }\mu\text{m}$) and a Mini Particle Sampler (MPS[®]; Ecomasure Inc. France) [31]. The operation conditions of these instruments are as follows: CPC flow rate of 1.5 l/min with 1 s of sampling time; SMPS flow rate of 0.3 l/min with 120 s of sampling time; APS-flow rate of 5 l/min with 5 s of sampling time).

A MPS is used for the particle collection through filtration technique on copper mesh grids (Model S143-3; Quantifoil Micro Tools GmbH Germany) which can be used later in Transmission Electron Microscope (TEM; Model CM12; Philips, The Netherlands) for various qualitative analyses of the released particles without any limitation on the aerosol size.

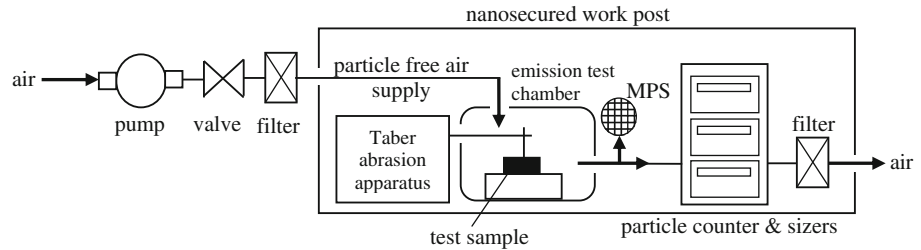
Therefore, the whole aerosol measurement section, quantifying the particle release, can measure aerosol particles having sizes ranging from 4 nm to $20\text{ }\mu\text{m}$. The deposition probability of this particle size range varies from 20 to 90% once they enter inside a human body [32]. For the analysis of the surfaces, a scanning electron microscope (QUANTA ESEMTM 400, FEI Inc. The Netherlands) has also been used.

2.5 Background and Particle Loss

Three empty test runs were done before the real experiment to measure the concentration of the background particles (particles present in the ambience of the experimental setup) and those generated by the motor of the abrasion apparatus. The abrasion apparatus was made to operate without the sample present in the chamber. The average concentration detected by CPC was $\sim 0.7\text{ cm}^{-3}$ with a standard deviation of 0.2 cm^{-3} in the whole volume. Therefore, the concentrations of all the background particles and those generated by the abrasion apparatus were insignificant. The calculations of the loss of particle concentration due to their deposition on the walls of the chamber have shown a loss of 4% in number during 10 min (equal to the duration of the abrasion process).

There can be some deposition and diffusion losses of the released particles in the connection tubes too. As a result of these losses, the values of the number concentrations of the aerosol particles, indicated by the instruments, may be somehow lower than the actual values. For the present work, five potential particle loss mechanisms

Fig. 3 Experimental setup



are considered: gravitational settling; diffusional deposition; turbulent inertial deposition; inertial deposition at a bend; inertial deposition at flow constrictions. The simplified equations, formulating these losses, are presented in the “Appendix.” For details on these mechanisms, the readers are encouraged to refer to [33]. Consequently, the values indicated by the instruments have been treated with the correction factors accounting for the estimated particle loss in the connection tubes. For particles having size 10 nm, the estimated theoretical loss is 17 % which gets reduces to less than 1 % for 100 nm and above. Such an approach ensures a more quantitative particle measuring system.

3 Theory

It is generally agreed that when two surfaces are pressed together in sliding contact, real contact occurs only at the tips of surface asperities where the material removal happens through either of the two ways: plastic flow or fracturing of the surface asperities. The dominating way

out of these two can be find out using plasticity index (ψ) of the system. It can be calculated according to the Eq. 1 [34].

$$\psi = \frac{E^*}{H_s} \left(\frac{\sigma^*}{r} \right)^{1/2} \quad (1)$$

In Eq. 1, $\frac{1}{E^*} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_A^2}{E_A}$, E_s and E_A are the elastic moduli of the brick substrate and the abrasant, respectively, ν_s and ν_A are the Poisson’s ratio of the brick substrate and the abrasant, respectively, H_s is the Vickers hardness number of the brick, σ^* is the standard deviation of the brick asperities’ heights and r is their RMS roughness. The plasticity index has been calculated for the present system using $E_A = 375$ GPa, $\nu_A = 0.1$ and the values shown in Table 1. It is equal to 2×10^{-11} . As suggested by [34], plastic flow of a system upon deformation is favored by high value of plasticity index ($\psi \geq 1$). Therefore, $\psi = 2 \times 10^{-11}$ is a very insignificant value for the plastic flow to occur. This observation suggests the material removal through fracturing. This estimation is also quite evident from the brittle nature of the brick.

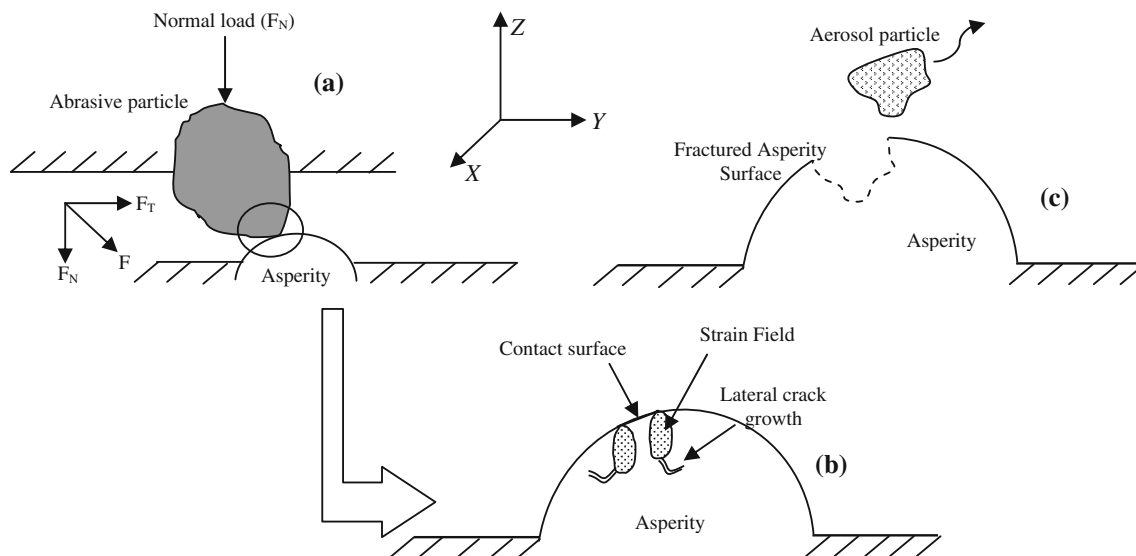


Fig. 4 **a** Real stress conditions under the effect of normal and shear forces; **b** strain field generation and fracture nucleation; **c** material removal via asperity fracturing

Figure 4 mimics the contact between an abrasive grain (present on the surface of the abradant) and an asperity (present on the surface of the brick) during abrasion and material removal due to fracturing. An asperity can be considered as a brittle solid subjected to a normal load (F_N) and a tangential force (F_T). Under the effect of these forces, a contact surface is developed between the abrasive grain and asperity surface (Fig. 4a). Inside the boundary of this surface, a uniform distribution of the compressive stresses is believed to develop with tensile stress of infinite magnitude at the edges of the boundary. These tensile stresses may give rise to very high elastic strain fields at the edges. When the stress being applied due to this strain field passes a certain limit (depending on the material), a crack is hypothesized to develop for relieving the excess stress. The strain fields and crack development over a zoomed view of the asperity are shown in Fig. 4b. Consequently, the crack propagates and leads to the material removal via fracturing (Fig. 4c).

4 Results and Discussion

4.1 Effect of F_N on the Total Wear Mass

In Fig. 5, the evolution of the total wear mass of the brick (M_t) with F_N is shown. M_t has been measured by measuring the mass of the brick before and after abrasion using a digital balance with a measurement precision of 0.001 g. This evolution appears to follow a linear path up to $F_N = 10.5$ N after which it unexpectedly increases for the higher loads. The standard deviations, measured in the values of the worn mass, ranged from 0 to 0.023 g.

It should be noted that the worn mass of the abradant was also measured simultaneously in the same way as that of the brick. It was found that after each abrasion test, the

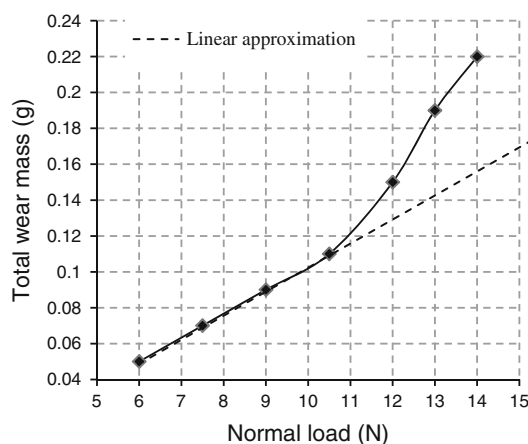


Fig. 5 Variation of the total wear mass of the brick with increasing normal load

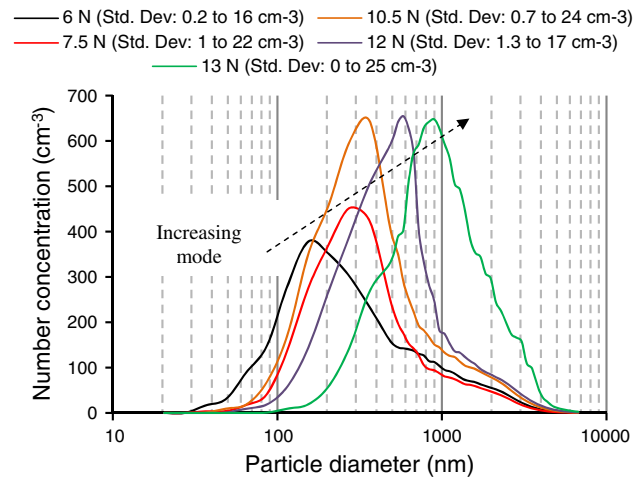


Fig. 6 Particle size distribution of the aerosol particles as a function of normal load

abradant lost less than 2 % of the worn mass of the brick which will thus be neglected.

4.2 Effect of Normal Load on the Released Aerosol Particle Concentration

In Fig. 6, the unimodal particle size distributions of the released aerosol particles (as measured by SMPS and APS) are shown for different normal loads. For each normal load, the abrasion test has been repeated thrice. With an increasing normal load, the mode of the size distribution is also increasing. However, beyond 10.5 N, the number concentration peak or the maximum particle number concentration remains at $\sim 645 \text{ cm}^{-3}$.

In Fig. 7, the evolution of the total number concentration of the aerosol wear particles is shown with respect to the normal load. For the particles having sizes in the range of 20–500 nm (measured using SMPS), it appears to increase up to 10.5 N of the normal load after which it starts decreasing. For 0.5–20 μm size range (measured using APS), it increases continuously. However, it seems to approach a constant value beyond 10.5 N.

Figure 8 shows the TEM analysis of the sampled aerosol particles which were collected on a mesh grid during abrasion at 4 different values of F_N . The aerosols appear to have irregular shapes with a high degree of polydispersion. The chemical analysis of these aerosol particles was found to have a Ti content of 5–7 % (in mass). The other dominating elements were Si (50–70 % in mass), Ca (8–10 % in mass) and Al (10–20 %).

The sizes of 50 different aerosol particles were measured for each grid, and their average sizes were determined in each case. Table 3 shows the average values. A clear increase in the average size of the sampled aerosol particles can be seen with the increasing F_N .

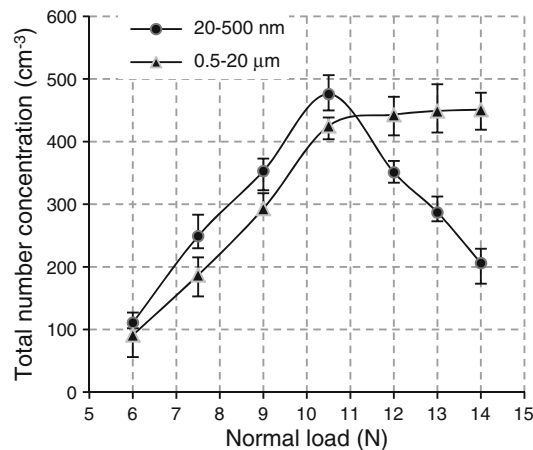


Fig. 7 Total number concentration of the aerosol particles as a function of normal load

Hence, from Figs. 5, 6, 7, 8 and Table 3, one can say that when $F_N \leq 10.5$ N, the wear mass is mainly composed of smaller-sized aerosol particles (<365 nm). Beyond 10.5 N, more and bigger-sized aerosol particles start being generated. In the latter case, most of the particles have more tendency to deposit on the surface as debris rather than to aerosolize. Also, when $F_N \leq 10.5$ N, it is believed by the authors that the fracturing of the surface asperities take place in such a way that it favors the generation of lower wear mass and smaller-sized particles. Such a case can be imagined if the fracture passes through the asperity, thus, disintegrating it in a number of smaller fragments. This can be compared with a trans-granular

Table 3 Average aerosol particle size of the sampled aerosol particles at different values of F_N

F_N (N)	6	9	10.5	13
Average aerosol particle size (μm)	0.2	0.9	3	5

fracture in crystalline solids. But when $F_N > 10.5$ N, it is believed that the fracturing of the surface asperities take place in such a way that it favors the generation of higher wear mass and bigger-sized aerosol particles. The concentration of the smaller-sized aerosol appears to either remain constant or decrease. Such a case can be imagined if the fracture passes along the boundary of the asperities, thus, cutting them out of the surface. This can be compared with an inter-granular fracture in crystalline solids.

5 Conclusions

Material removal mechanism through fracture has been understood via a schematic representation.

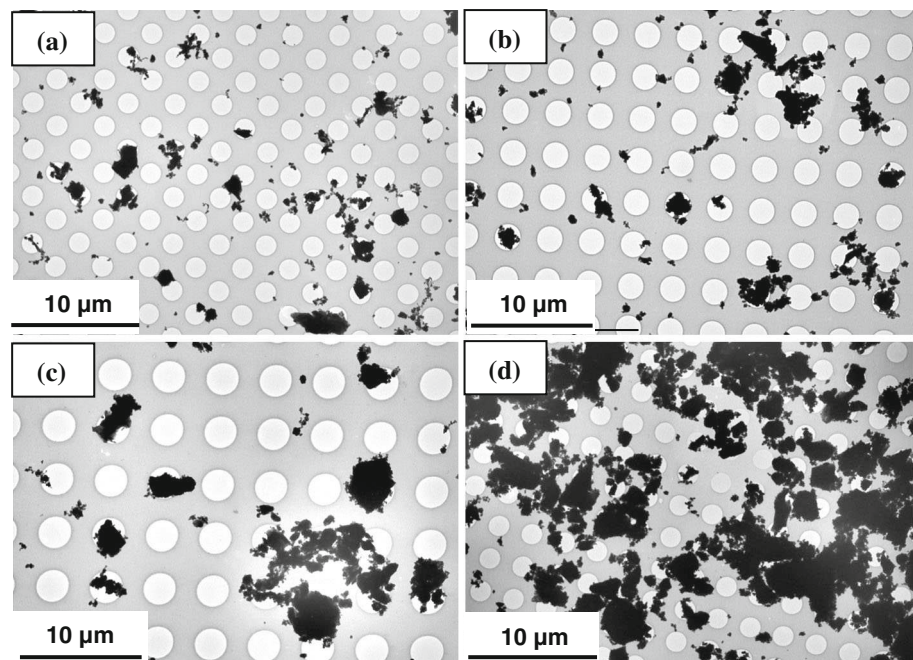
The normal load was observed to be a critical parameter in deciding the total wear mass and size of the resulting aerosol particles.

The released aerosol particles were polydispersed and had an irregular shape.

There was some Ti content in the released aerosol particles (5–7 % in mass).

At lower normal loads (≤ 10.5 N), the total wear mass was increasing linearly and beyond this point, it had an unexpected increase (Fig. 5).

Fig. 8 TEM image of the aerosol particles collected during abrasion at **a** $F_N = 6$ N; **b** $F_N = 9$ N; **c** $F_N = 10.5$ N; **d** $F_N = 13$ N



The size of the aerosol particles increased with the increase in normal load. However, their number concentration either decreased or attained a constant value (Figs. 6, 7 and 8).

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Appendix

Expressions used in calculating the particles loss during transportation using tubes.

1. Transport efficiency in case of gravitational settling of the particles:

$$\sigma_{\text{tube,grav}} = 1 - \frac{2}{\pi} \left[2\psi \sqrt{1 - \psi^{2/3}} - \psi^{1/3} \sqrt{1 - \psi^{2/3}} + \sin^{-1}(\psi^{1/3}) \right]$$

$$\psi = \frac{3L}{4d} \frac{V_{\text{ts}}}{U} \cos \theta$$

$$V_{\text{ts}} = \frac{\rho_p d_p^2 g C_c}{18\eta}$$

$$C_c = 1 + \frac{1}{Pd_p} [15.6 + 7 \exp(-0.059Pd_p)]$$

2. Transport efficiency in case of diffusional deposition of the particles:

$$\sigma_{\text{tube,diff}} = \exp\left(\frac{-4V_{\text{dep}}L}{dU}\right)$$

$$V_{\text{dep}} = \frac{0.04\bar{U}}{Re^{1/4}} \left(\frac{\rho_g D}{\eta}\right)^{2/3}$$

3. Transport efficiency in case of turbulent inertial deposition of the particles:

$$\sigma_{\text{tube,turbintert}} = \exp\left(\frac{-\pi dLV_t}{Q}\right)$$

4. Transport efficiency in case of inertial deposition of the particles at a bend:

$$\sigma_{\text{bend,inert}} = 1 - Stk\varphi$$

$$\sigma_{\text{bend,inert}} = \exp(-2.823Stk\varphi)$$

$$Stk = \frac{\tau U}{d}$$

5. Transport efficiency in case of inertial deposition of the particles at flow constrictions:

$$\sigma_{\text{bend,inert}} = 1 - \frac{1}{1 + \left\{ \frac{2Stk \left[1 - \left(\frac{d_p}{d_i} \right)^2 \right]}{3.14 \exp(-0.0185\theta)} \right\}^{-1.24}}$$

References

1. Behfarnia, K., Keivan, A., Keivan, A.: The effects of TiO₂ and ZnO nanoparticles on physical and mechanical properties of normal concrete. *Asian J. Civil Eng. (BHRC)* **14**, 517–531 (2013)
2. Jalal, M., Fathi, M., Farzad, M.: Effects of fly ash and TiO₂ nanoparticles on rheological, mechanical, microstructural and thermal properties of high strength self compacting concrete. *Mech. Mater.* **61**, 11–27 (2013)
3. Bhuvaneshwari, B., Sasmal, S., Baskaran, T., Iyer, N.R.: Role of nano oxides for improving cementitious building materials. *J. Civil Eng. Sci.* **1**, 52–58 (2012)
4. Stamate, M., Lazar, G.: Application of titanium dioxide photocatalysis to create self-cleaning materials. *Rom Tech Sci Acad MOCM* **13–3**, 280–285 (2007)
5. Fujishima, A., Hashimoto, K., Watanabe, T.: TiO₂ photocatalysis: fundamentals and applications, 1st edn. BKC, Tokyo (1999)
6. Torgal, F.P., Jalali, S.: Eco-efficient construction and building materials. *Constr. Build. Mater.* **25**, 582–590 (2011)
7. Vorbau, M., Hillemann, L., Stintz, M.: Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings. *Aerosol Sci.* **40**, 209–217 (2009)
8. Suzuki, S., Ando, E.: Abrasion of thin films deposited onto glass by Taber test. *Thin Solid Films* **340**, 194–200 (1999)
9. Shandilya, N., Le Bihan, O., Morgeneyer, M.: A review on the study of the generation of (nano-) particles aerosols during the mechanical solicitation of materials. *Nanomaterials Art. ID 289108* (2014)
10. Lee, J., Mahendra, S., Alvarez, P.P.J.: Nanomaterials in the construction industry: a review of their applications and environmental health and safety considerations. *ACS Nano* **4**, 3580–3590 (2010)
11. Le Bihan, O., Shandilya, N., Gheerardyn, L., Guillon, O., Dore, E., Morgeneyer, M.: Investigation of the release of particles from a nanocoated product. *Adv. Nanoparticles* **2**, 39–44 (2013)
12. Shandilya, N., Le Bihan, O., Bressot, C., Morgeneyer, M.: Evaluation of the particle aerosolization from n-TiO₂ photocatalytic nanocoatings under abrasion. *Nanomaterials* **2014**, 185080 (2014). doi:10.1155/2014/185080
13. Petkovic, J., Zegura, B., Stevanovic, M., Drnovsek, N., Uskokovic, D., Novak, S.: DNA damage and alterations in expression of DNA damage responsive genes induced by TiO₂ nanoparticles in human hepatoma HepG2 cells. *Nanotoxicology* **5**, 341–353 (2011)
14. Unnithan, J., Rehman, M.U., Ahmad, F.J., Samim, M.: Aqueous synthesis and concentration-dependent dermal toxicity of TiO₂ nanoparticles in Wistar rats. *Biol. Trace Elem. Res.* **143**, 1682–1694 (2011)
15. Warheit, D.B., Brock, W.J., Lee, K.P., Webb, T.R., Reed, K.L.: Comparative pulmonary toxicity inhalation and instillation studies with different TiO₂ particle formulations. *Toxicol. Sci.* **88**, 514–524 (2005)
16. Soo, J.C., Tsai, P.J., Chen, C.H., Chen, M.R., Hsu, H.I., Wu, T.N.: Influence of compressive strength and applied force in concrete on particles exposure concentrations during cutting processes. *Sci. Total Environ.* **409**, 3124–3128 (2011)

17. Zimmer, A.T., Maynard, A.D.: Investigation of the aerosols produced by a high speed, hand held grinder using various substrates. *Ann. Occup. Hyg.* **46**, 663–672 (2002)
18. Wahlström, J., Olander, L., Olofsson, U.: A pin-on-disc study focusing on how different load levels affect the concentration and size distribution of airborne wear particles from the disc brake materials. *Tribol. Lett.* **46**, 195–204 (2012)
19. ASTM International: Standard Test Method for the Abrasion of Organic Coatings by the Taber Abraser. ASTM D4060 (2007)
20. ASTM International: Standard Test Methods for Dry Abrasion Mar Resistance of High Gloss Coatings. ASTM D6037 (1996)
21. ASTM International: Standard Test Method for Resistance of Transparent Plastics to Surface Abrasion. ASTM D1044 (2008)
22. Boentoro, W., Pflug, A., Szyszka, B.: Scratch resistance analysis of coatings on glass and polycarbonate. *Thin Solid Films* **517**, 3121–3125 (2009)
23. Sepeur, S., Kunze, N., Werner, B., Schmidt, H.: UV curable hard coatings on plastics. *Thin Solid Films* **351**, 216–219 (1999)
24. Katsamberis, D., Browall, K., Iacovangelo, C., Neumann, M., Morgner, H.: Highly durable coatings for automotive polycarbonate glazing. *Prog. Org. Coat.* **34**, 130–134 (1998)
25. Wank, A., Wielage, B., Pokhmurska, H., Friesen, E., Reisel, G.: Comparison of hardmetal and hard chromium coatings under different tribological conditions. *Surf. Coat. Tech.* **201**, 1975–1980 (2006)
26. Huang, C.-Y., Tseng, C.-I.: The effect of interface modification between POM and PTFE on the properties of POM/PTFE composites. *Appl. Polym. Sci.* **78**, 800–807 (2000)
27. Morgeneyer, M., Shandilya, N., Chen, Y.-M., Le Bihan, O.: Use of a modified Taber abrasion apparatus for investigating the complete stress state during abrasion and in-process wear particle aerosol generation. *Chem. Eng. Res. Des.* (2014). doi:[10.1016/j.cherd.2014.04.029](https://doi.org/10.1016/j.cherd.2014.04.029)
28. Morgeneyer, M., Le Bihan, O., Ustache, A., Aguerre Chariol, O.: Experimental study of the aerosolization of fine alumina particles from bulk by a vortex shaker. *Powder Technol.* **246**, 583–589 (2013)
29. Le Bihan, O., Ustache, A., Bernard, D., Aguerre Chariol, O., Morgeneyer, M.: Experimental study of the aerosolization from a carbon nanotube bulk by a vortex shaker. *Nanomaterials* **2014**, 193154 (2014). doi:[10.1155/2014/193154](https://doi.org/10.1155/2014/193154)
30. Le Bihan, O., Morgeneyer, M., Shandilya, N., Aguerre Chariol, O., Bressot, C.: Handbook of nanosafety-measurement, exposure and toxicology. In: Vogel, U., Savolainen, K., Wu, Q., Van Tongeren, M., Brouwer, D., Berges, M. (eds.) *Emission Chambers: A Method for Nanosafety*, 1st edn, pp. 226–231. Academic Press, Elsevier Inc., San Diego (2014)
31. R'mili, B., Le Bihan, O., Dutouquet, C., Aguerre Charriol, O., Frejafon, E.: Particle sampling by TEM grid filtration. *Aerosol Sci. Technol.* **47**, 767–775 (2013)
32. Oberdörster, G., Oberdörster, E., Oberdörster, J.: Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. *Environ. Health Perspect.* **113**, 823–839 (2005)
33. Brockmann, J.E.: Aerosol measurement-principles, techniques and applications. In: Kulkarni, P., Baron, P.A., Willeke, K. (eds.) *Aerosol Transport in Sampling Lines and Inlets*, 3rd edn, pp. 69–103. Wiley, Hoboken, NJ (2011)
34. Hutchings, I.M.: *Tribology-Friction and Wear of Engineering materials*. CRC Press, Cambridge (1992)

5.2 Emission from nanocoatings

After considering the TiO₂ nanoparticles reinforced bricks for determining their ENM emission tendency in the first case study, the second case study considers the photocatalytic nanocoatings which also contain TiO₂ nanoparticles. These types of nanocoatings are a perfect example of the modern innovations in materials technology introduced through nanotechnology. In the real life, they are normally applied on the external surfaces of the buildings for the protection of the surfaces from the atmospheric dust particles and thus improve their appearance and durability.

Two commercial nanocoatings- Tipe X503[®] and Photocal Masonry[®], are selected for this study. In real life, they find their primary use over the porous masonry surfaces. The findings of our study are presented through the following article, entitled “Evaluation of the particle aerosolization from n-TiO₂ photocatalytic nanocoatings under abrasion”.

In this article, these two nanocoatings are referred as Nanocoating 1 and Nanocoating 2 respectively for confidentiality purposes. The article is important in knowing the nature, size and shape in which the aerosols of TiO₂ nanoparticles get emitted as a function of the type of the nanocoating, its number of layers and the level of the mechanical stresses to which they are subjected to. The results suggest that out of the two nanocoatings, Photocal Masonry efficiently inhibits the aerosol emission. This inhibition gets further efficient with the increase in the number of layers. However, the emitted aerosols were found to be comprising of the particles having ENM embedded inside the nanocoating polymer matrix. In the same article, a conceptual model characterizes the particles emission behavior in the case of these nanocoatings, compares it with an uncoated substrate and puts forward indicators to evaluate the nanocoatings’ performance qualitatively.

Hence, in this article, the effect of applying the mechanical stress alone (via abrasion) is shown. In the next case study, this mechanical stress is coupled with the accelerated environmental weathering, with varying durations, to observe the change which this coupling might induce on the quantity and quality of the generated aerosol particles.

Research Article

Evaluation of the Particle Aerosolization from n-TiO₂ Photocatalytic Nanocoatings under Abrasion

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A parametric study on the release of titanium dioxide (TiO₂) nanoparticles from two commercial photocatalytic nanocoatings is carried out. For this, abrasion tests are performed on them. The formed aerosols are characterized by their number concentration, particle size distribution, individual particle shape, size, and chemical composition. The two nanocoatings appear to exhibit contrastingly opposite behavior with respect to the number concentration of the released particles. Having irregular shapes, the released particles are found to have unimodal size distributions with 1.5–3.5% (in mass) of Ti content. However, no free nanoparticles of TiO₂ were found. Distinct phases during the particle number concentration evolution with time are also discussed and evaluated. Two quantities— $(\Delta C/\Delta t)_I$ and T_{II} —are identified as the important indicators to qualitatively measure the resistance strength and hence the concentration of the released particles from a nanocoating during stress application.

1. Introduction

Photocatalytic nanocoatings are the special type of coatings that accelerate the reaction of forming activated oxygen from water or oxygen in the air. It accomplishes this formation by capturing ultraviolet light in the presence of photocatalyst titanium dioxide (TiO₂) nanoparticles [1, 2]. The formed activated oxygen is strong enough to oxidize and decompose organic materials and kill bacteria. As a result, these nanocoatings impart self-cleaning, air purifying, antibacterial, odor destructive, and super hydrophilic and antistatic (resistance of the static adsorption of small dust particles) properties to the surfaces on which they are applied. Such advantages have rendered their increasing use in construction or masonry applications like walls, pavements, and so forth [1–3]. However, during their lifecycle, these nanocoatings are subjected to various mechanical stresses in the form of the handling or processing of the parts coated with them [4–10]. This may result in their disintegration and the TiO₂ nanoparticles may start to get released in air in the form of aerosol [11, 12]. Upon exposure, these released TiO₂ nanoparticles may interact with the human organism

through inhalation or dermal contacts and get deposited inside the body. Various toxicological studies have demonstrated toxic effects of some types of TiO₂ nanoparticles in this case [13–15]. In spite of this, there is no sufficient information in the literature about the possible release of nanoparticles from photocatalytic nanocoatings. To better understand this, nanoparticle aerosol release evaluation is critical.

The study presented here aims to evaluate aerosol particle release or aerosolization from two commercial photocatalytic nanocoatings having nanoparticles of TiO₂. For simulating the stress conditions to which such coatings are subjected to, their abrasion is done. An experimental set-up is developed where the particles, after getting generated from abrasion, are characterized by aerosol measurement devices both in qualitative and semiquantitative ways.

2. Materials and Method

2.1. Surface Coating Material. For the study, two different commercially available photocatalytic nanocoatings were chosen. The details on the material properties are provided in

TABLE 1: Material properties of the two nanocoatings (data provided by the manufacturers).

Properties	Nanocoating 1	Nanocoating 2	Uncoated brick
Main composition	Nanotitanium Dioxide	Nanotitanium dioxide	Al, Si, Ca
Crystallite structure	Anatase	Anatase	—
Average primary particle size	<8 nm	<40 nm	7 μm (r.m.s. roughness)
Coagulation index	~2	~4	—
Appearance	Pale white liquid	Yellowish transparent liquid	Yellow
Dispersant	Water-based	Water-based	—
TiO ₂ vol. %	1.1	1	—

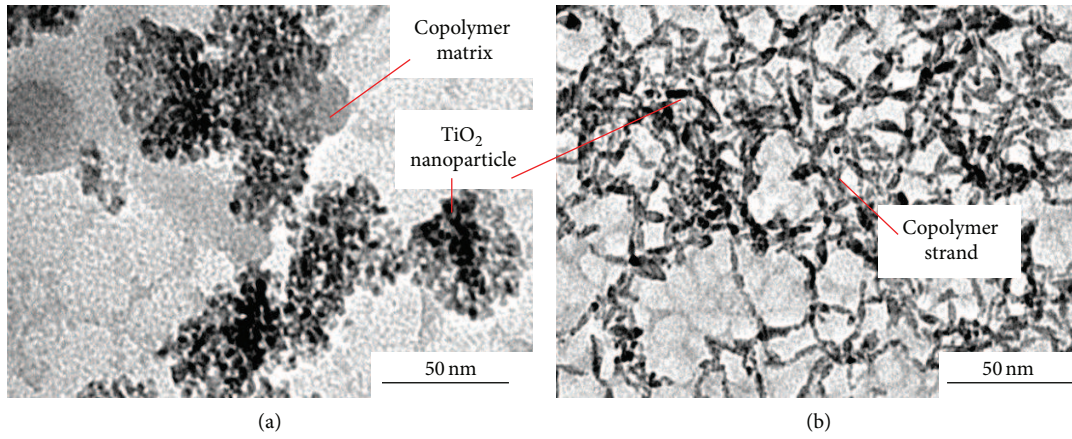


FIGURE 1: Microscopic analyses of the morphology of the nanoparticles present in the (a) nanocoating 1 and (b) nanocoating 2.

Table 1. The substrate chosen for the nanocoating application was a masonry brick (11 cm $\times$ 5 cm $\times$ 5 cm; Leopard brick, Ref: 901796, Castorama). It is basically an aluminosilicate brick which is frequently used in constructing façades, house walls, stairs, and so forth.

To evaluate the elemental composition and the constituent nanoparticles' morphology of the two nanocoatings, a transmission electron microscopy (TEM; Model CM12; Philips, The Netherlands) analysis was done. For this, two separate 1% (by volume) diluted solutions of the two nanocoatings were prepared. One drop (8 μL approximately) was taken from each diluted solution and was deposited on TEM copper mesh grids (Model S143-3; Quantifoil Micro Tools GmbH Germany). These mesh grids were made hydrophilic by their plasma treatment—0.1 mbar, 45 mA, 3 min—(Model K100X, Glow Discharge, Emitech, Quorum Technologies Ltd. UK) prior to drop deposition. After the deposition, the grids were then allowed to dry in a closed chamber so that the water content gets evaporated and the TiO₂ nanoparticles rest deposited on the grid.

In Figures 1(a) and 1(b), TEM images of the dried grids are shown. In Figure 1(a), the two phase agglomerates of the deposited particles from nanocoating 1 can be observed. These two phases are believed to be contributed by the copolymer (in grey color) and TiO₂ nanoparticles (in pitch black color). The average TiO₂ particle size is measured to be 8 ± 4 nm. However, in Figure 1(b), a network of stranded like structures from nanocoating 2 can be seen in which TiO₂ nanoparticles (appearing as small black chunks) are believed

to be embedded in copolymer strands. With a two phased structure, the average TiO₂ particle size is measured to be 25 ± 17 nm. The energy-dispersive X-ray analysis (EDX; Model X-max; Oxford Instruments UK) of the elemental composition of both nanocoatings shows similar chemical compositions, that is, C (60 to 65% in mass), O (15 to 20% in mass), Ti (10 to 15% in mass), Si (0 to 2% in mass), and traces of Al (<1% in mass).

The substrate surface preparation and the nanocoating application were done according to the technical data sheet recommended by the nanocoating manufacturers (i.e., degreased using brush and ethanol soaked paper, dry, and dust free surfaces; use of a high volume low pressure spray during coating; 25°C of ambient temperature). Different coating samples were prepared with two and four layers of both nanocoatings.

2.2. Abrasion Process. The standard Taber linear abrasion apparatus (Model 5750; Taber Inc. USA) was used for the abrasion of the nanocoatings. The apparatus is referenced in numerous internationally recognized test standards [16–18]. This apparatus is already being used in industries for analyzing the performance of products like paint, coating, metal, paper, textile, and so forth, during the application of a mechanical stress [19]. The stress being applied through Taber also corresponds to the typical one applied to surface coatings in a domestic setting, for example, walking with shoes and displacement of different objects [4, 7]. It incorporates

TABLE 2: Experimental parameters (repetition of the tests: 3 times).

Test sample	Number of layers of nanocoating (NOL)	Normal load			Abradant	Stroke length (mm)	Abrasion speed (cpm)	Number of cycles
		6 N	7.5 N	10.5 N				
Uncoated (reference)	0	X	X	X				
Nanocoating 1	2	X	X	X	H38	76	60	600
	4	X	X	X				
Nanocoating 2	2	X	X	X				
	4	X	X	X				

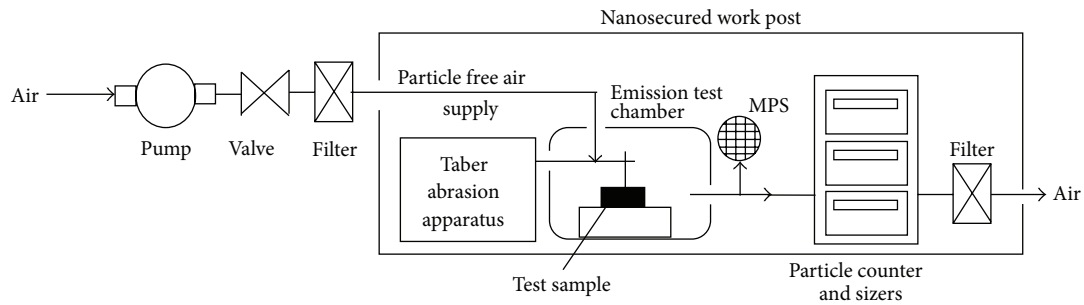


FIGURE 2: Experimental set-up.

a motor driven horizontal arm/bar that displaces an abradant in a back and forth linear motion over the test sample. The abrasion is caused by the friction at the contact surface between the surfaces of the abradant and the sample. Via a vertical shaft, a known weight is mounted on the top of the abradant which shall be referred to as the *Normal Load* in the text. The abrasiveness can be varied by changing the type of the abradant and normal load value. It is imperative to apply a reproducible and standardized stress on the test samples for reproducible tests. This has been ensured through preliminary tests and contextual literature survey on the optimal adjustment of the Taber abrasion apparatus [20–24].

2.3. Parameters Studied. In total, the effect of three experimental parameters on the concentration of released aerosol particles was studied: type of the nanocoating (i.e., nanocoatings 1 and 2), normal load (i.e., 6, 7.5, and 10.5 N), and number of layers of the nanocoating (i.e., 2 and 4).

The details can be seen in Table 2. An uncoated brick sample was also used for the reference. A Taber H38 nonresilient vitrified clay-carborundum abradant was used during the whole study [25]. The abrasion stroke length, abrasion speed, abrasion duration, and the number of abrasion cycles were kept constant at 76 mm, 60 cycles per minute (cpm), 10 min, and 600, respectively.

2.4. Experimental Set-Up. Figure 2 shows the scheme of the complete experimental set-up. Particle free air is passed through a nanosecured work post (HPPE 10, Erma Flux S.A., France) [26] containing the Taber abrasion apparatus. This work post has a particle filter efficiency of 99.99%. The test sample is placed inside a self-designed *Emission Test Chamber* (0.5 m × 0.3 m × 0.6 m) [27]. A slot is provided

on one of the walls of this chamber allowing the horizontal arm of abrasion apparatus passing through and operating the apparatus (equipped with motor) to be placed externally. The sampling of the generated aerosol particles is done in a close proximity of the test sample. The Taber apparatus along with the emission test chamber constitute aerosol generation section. The aerosol particles, getting generated during the abrasion process, are characterized in terms of their number concentration and number size distribution. The aerosol generation section is combined with an aerosol measurement section. It consists of a condensation particle counter (CPC; Model 3775; TSI Inc. USA; measurable size range: 4 nm to 3 μm), a scanning mobility particle sizer (SMPS; Model DMA 3081 and CPC 3775; TSI Inc. USA; measurable size range: 15 to 500 nm), an aerodynamic particle sizer (APS; Model 3321; TSI Inc. USA; measurable size range: 0.5 to 20 μm), and a miniparticle sampler (MPS; Ecomasure Inc. France) [28, 29]. The operation conditions of these instruments are as follows: CPC-flow rate of 1.5 L/min with 1 s of sampling time; SMPS-flow rate of 0.3 L/min with 120 s of sampling time; APS-flow rate of 5 L/min with 5 s of sampling time.

A MPS is used for the particle collection through filtration technique on copper mesh grids which can be used later in TEM for various qualitative analyses of the released particles without any limitation on the aerosol size.

Therefore, the whole aerosol measurement section, quantifying the particle release, can measure aerosol particles having sizes ranging from 4 nm to 20 μm. The deposition probability of this particle size range varies from 20 to 90% once they enter inside a human body [30]. The whole experimental set-up, in general, follows the ones used in [4, 31, 32]. For the analysis of the surfaces, a scanning electron microscope (QUANTA ESEM 400, FEI Inc., The Netherlands) has also been used.

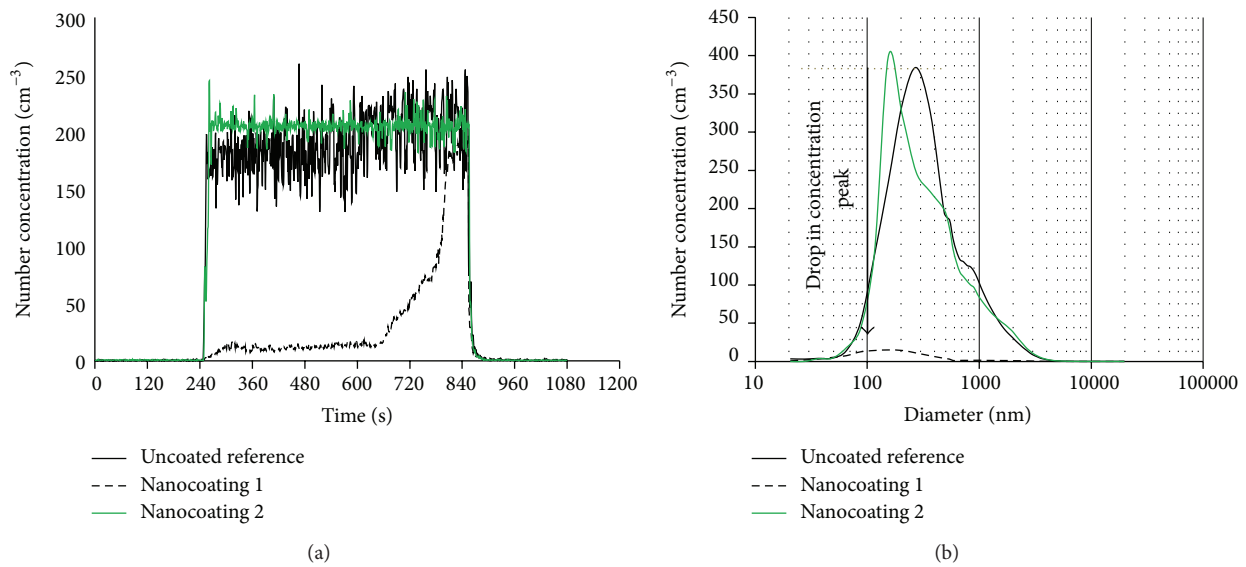


FIGURE 3: (a) Particle number concentration variation with time. (b) Size distribution of the aerosol particles generated during abrasion of 4 layered nanocoating samples under 6 N of normal load (note: all the curves are mean curves obtained from 3 repeated tests).

2.5. Background and Particle Loss. Three empty test runs were done before the real experiment to measure the concentration of the background particles and those generated by the abrasion apparatus. The abrasion apparatus was made to operate without the sample present in the chamber. The average concentration detected by CPC was $\sim 0.7 \text{ cm}^{-3}$ with a standard deviation of 0.2 cm^{-3} in the whole volume. Therefore, the concentrations of all the background particles and those generated by the abrasion apparatus were insignificant. The calculations of the loss of particle concentration due to their deposition on the walls of the chamber have shown a loss of 4% in number during 10 min (equal to the duration of the abrasion process).

Along with some turbulence losses, there can be some particle loss in the transport tubes also. These losses have not been taken into account while calculating the particle number concentrations. Hence, the present study is rather semiquantitative.

3. Results

3.1. Effect of the Type of Nanocoating. Figures 3(a) and 3(b) compare, through an example, the particle number concentration curves produced when the 4 layered nanocoating test samples were abraded under a normal load of 6 N. The test was repeated thrice under same conditions. For uncoated reference, the repetition was done on the same brick. In Figure 3(a), the abrasion starts at $t = 240 \text{ s}$ and ends at $t = 840 \text{ s}$. Before and after this time interval ($t = 0$ to 240 s), the system is idle.

The nanocoating 2 seems to impart no difference on the aerosol particle release when it is compared with the uncoated reference. The two have almost the same concentration levels. Since the nanocoating 2 probably gets rubbed off completely

without providing any resistance, the particle number concentration attains its maximum value ($C \approx 200 \text{ cm}^{-3}$) soon after the abrasion starts. The standard deviation ranges from 5 to 16 cm^{-3} .

For nanocoating 1, the number concentration is initially low ($C \approx 14 \text{ cm}^{-3}$) due to a probable resistance of the nanocoating 1 against abrasion. However, this resistance continues up to a certain point ($t = 624 \text{ s}$) after which the nanocoating 1 may start getting rubbed off. As a result, the number concentration starts increasing gradually. It attains the same value as for nanocoating 2 or the reference towards the end of the abrasion. The standard deviation in the values measured for nanocoating 1 varies from 0.7 to 27 cm^{-3} .

In Figure 3(b), the particle size distribution of the released aerosol particles, during the abrasion process, is shown. The nanocoating 2 seems to have no effect on the size distribution too. However, there is a shift of the size mode towards smaller particle sizes ($154 \pm 10 \text{ nm}$). The standard deviation in the particle size distribution values measured for nanocoating 2 changes from 0.2 to 16 cm^{-3} .

The nanocoating 1 considerably drops the peak of the number concentration curve by a factor of ~ 30 rendering the particle release totally insignificant. The standard deviation measured here is 8 cm^{-3} maximum.

In Figures 4(a) and 4(b), general overviews of the released particles are shown which were sampled during first 4 minutes of the abrasion test. A polydispersed aerosol from both nanocoating 1 (Figure 4(a)) and nanocoating 2 (Figure 4(b)) can be seen on the mesh grid with a high degree of agglomeration. A closer look on the morphology (Figure 4(c) for nanocoating 1 and Figure 4(d) for nanocoating 2) shows irregularly shaped aerosol particles having size ranging from hundreds of nanometer to tens of micrometer. The chemical analysis of these aerosol particles was found to have a Ti content of 1.5–3.5% (in mass) for both nanocoatings. However,

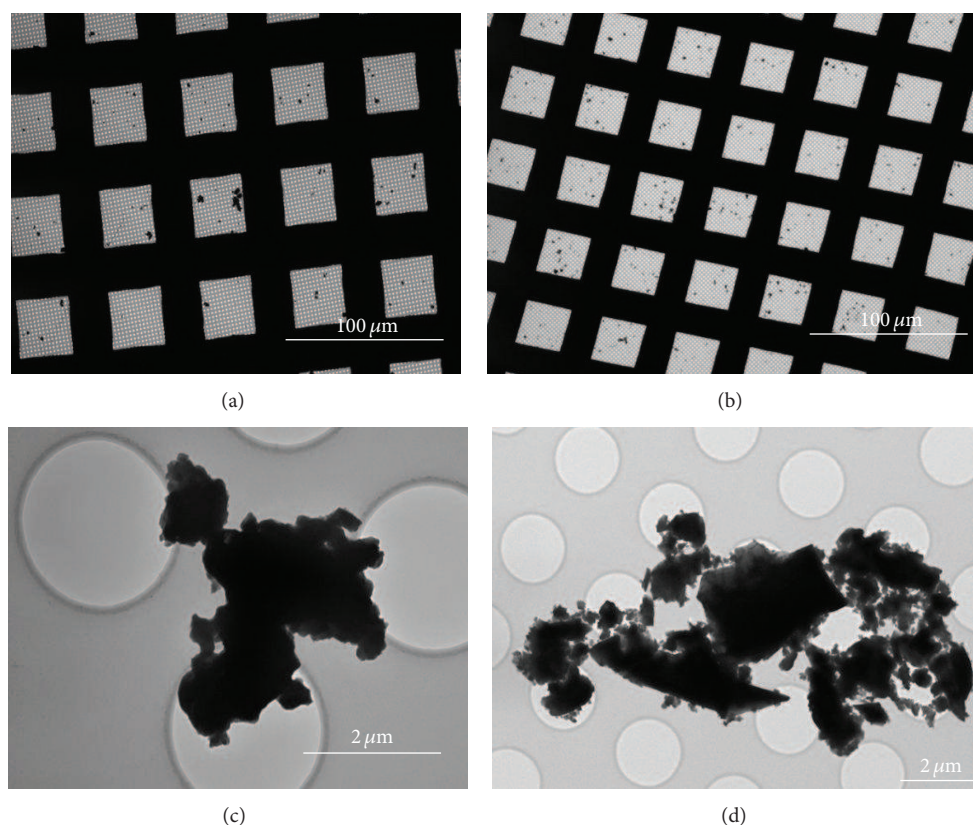


FIGURE 4: TEM image of the aerosol particles generated from (a) and (c) nanocoating 1 and (b) and (d) nanocoating 2.

the released aerosol particles from nanocoating 2 were found to be dominated by Si (50–70% in mass; essentially coming from the brick and the abradant), C (5–7% in mass; essentially coming from the nanocoating 2 copolymer), and Al (10–20%; essentially coming from the brick). In case of nanocoating 1, Al was completely missing from the elemental composition of the released aerosol particles and the C content was elevated by 4–5%.

Therefore, from these observations, one can say that in case of nanocoating 1, the release of the aerosol particles was entirely contributed by nanocoating 1 itself. No particles came from the brick underneath. But for nanocoating 2, presence of the Al shows that the aerosol particles came from the brick too after the nanocoating 2 deterioration. It should be noted that for both nanocoatings, no free particles of TiO_2 were found on the grid. In fact, they were found to be embedded inside the copolymer matrix of the nanocoatings.

3.2. Effect of the Normal Load. In Figure 5(a), effect of increasing normal load has been shown on a 4 layered nanocoating 1 sample. The abrasion commences at $t = 240$ s and ends at $t = 840$ s. For a clear view of the particle number concentrations, between $t = 240$ s and $t = 480$ s, a zoomed view in Figure 5(a1) is also shown. The released aerosol particle number concentration is found to be increasing with normal load. The same pattern continues in Figure 5(b) for a 4 layered nanocoating 2 sample too.

While measuring the particle size distribution in case of the nanocoating 1, the SMPS and APS showed very low concentrations which were even close to their particle detection thresholds. Hence, the two particle sizers were not employed further. But for nanocoating 2, there were no such problems. Thus, the size distribution, for nanocoating 2, is shown in Figure 5(c). Three unimodal distributions with increasing size modes (i.e., 154 nm to 274 nm to 365 nm) and increasing concentration peaks can be seen for increasing normal loads.

3.3. Effect of the Number of Layers. The number of layers also has a substantial effect on the aerosol particles generation. Figure 6 demonstrates this effect where two samples, having 2 and 4 layers of nanocoating 1, are tested under a normal load of 6 N. The abrasion commences at $t = 240$ s and ends at $t = 840$ s. The released particle number concentration is always lower when a 4 layered sample (std. deviation: 2 to 27 cm^{-3}) is abraded as compared to the two layered one (std. deviation: 13 to 37 cm^{-3}) or an uncoated reference. Both sets of layers seem to provide resistance towards abrasion. The SEM observations of the 4 layered nanocoating 1 sample were also done at the end of the abrasion. Figure 7 shows the observation. An unabraded coated surface (marked A) had an average Ti content of ~12% (in mass). For the abraded part (marked B), the average Ti content lowers down to ~0% (in mass), thus, completely exposing the brick surface. However,

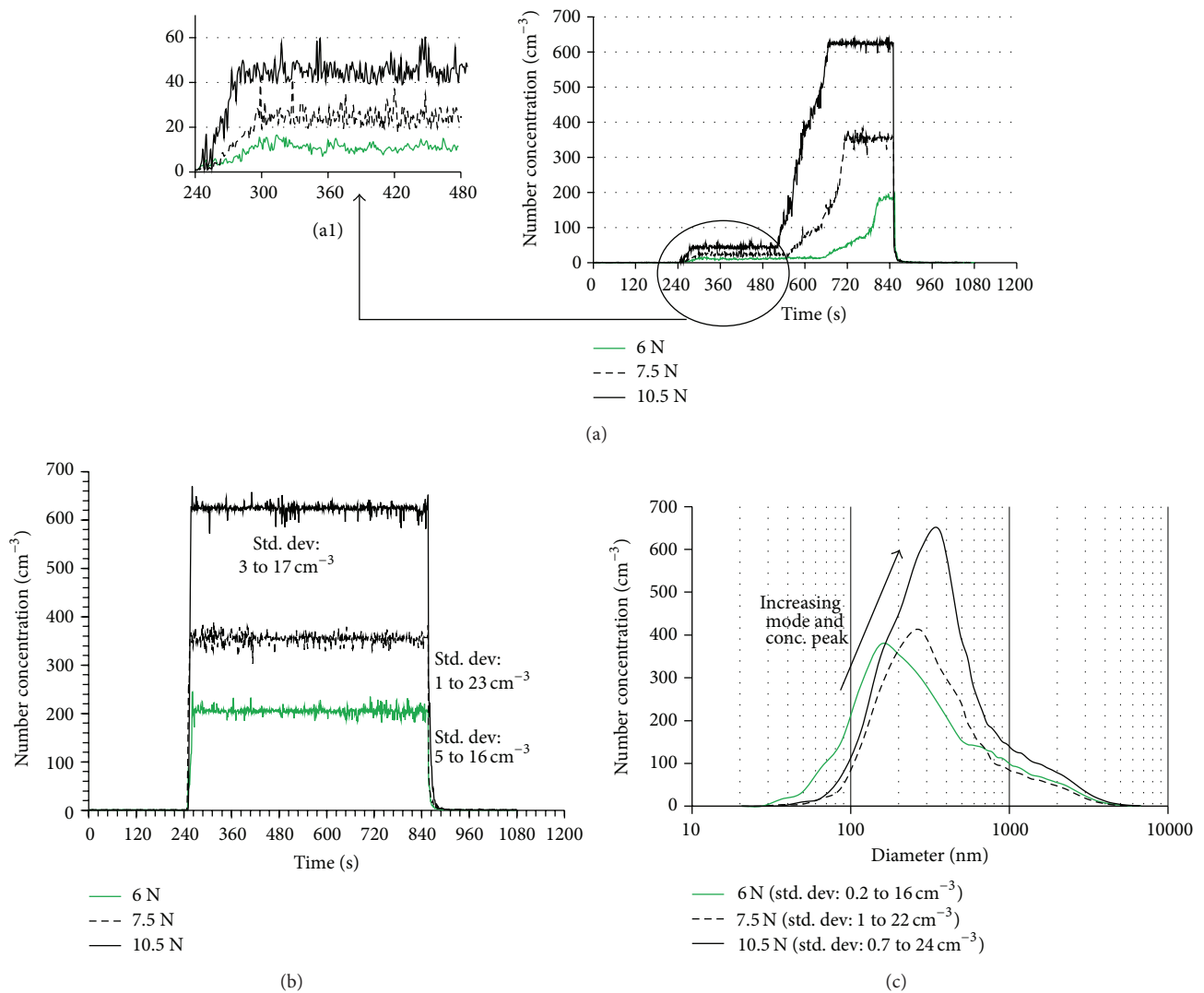


FIGURE 5: (a) Particle number concentration variation with time for 4 layered nanocoating 1 and (b) nanocoating 2 sample; (a1) zoomed view; (c) size distribution of the aerosol particles generated during abrasion of 4 layered nanocoating 2 sample (note: all the curves are mean curves obtained from 3 repeated tests).

in the case of nanocoating 2, both 2 and 4 layered samples had similar particle number concentrations.

4. Discussion

The particle number concentration ($\#C$) variations with time (t), shown in Figures 3(a) and 5(a), can be modeled in the forms shown in Figure 8 where Figure 8(a) corresponds to the uncoated reference, Figure 8(b) corresponds to the nanocoating 1, and Figure 8(c) corresponds to the nanocoating 2. Considering Figure 8(b), the curve for particle number concentration variation is constituted of 5 segments marked as EF, FG, GH, HI, and IJ.

The abrasion process starts at point E. As a result, $\#C$ starts rising from point E and stops at point F. This phase can be termed as *phase I*. During this phase, the contact surface conditions between the abrasant and the nanocoating are

believed to evolve due to changing surface roughness during abrasion. This evolution (marked as $(\Delta C_1/\Delta t)_I$) continues until the two surfaces come in equilibrium with each other which corresponds to point F. From the point F to the point G, $\#C$ remains constant, that is, *phase II*. During this phase, the abrasion of the nanocoating is being done under an equilibrium or stationary state and the nanocoating is still in a stable state. The EDX analysis of the nanocoating surface during this phase showed a strong presence of 5–8% (in mass) of Ti. There is some Ti content (~3.5% (in mass)) with no Al content in the sampled aerosol particles too (Figure 4(c)). From point G, $\#C$ rises again to the point H, that is, *phase III*. In this phase, the deterioration of the nanocoating is believed to start. The duration of this phase is decided by the level of the resistance a nanocoating can provide against its deterioration. Beyond point H, $\#C$ gets saturated and drops at point I (*phase IV*), where the abrasion stops. The nanocoating

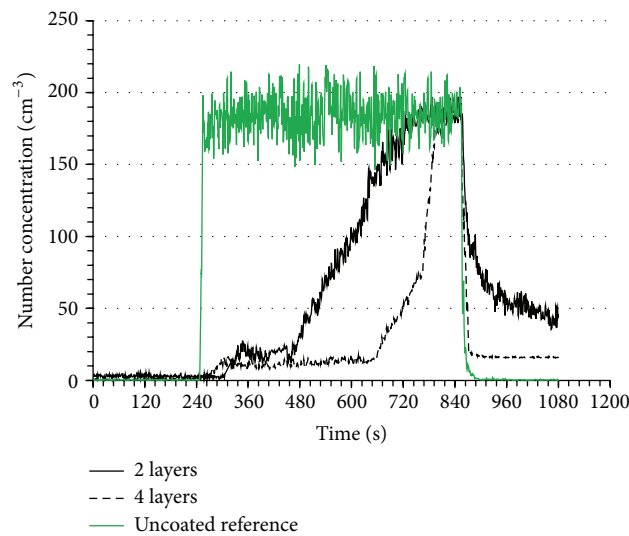


FIGURE 6: Particle number concentration variation with time for 2 and 4 layered nanocoating 1 samples (note: all the curves are mean curves obtained from 3 repeated tests).

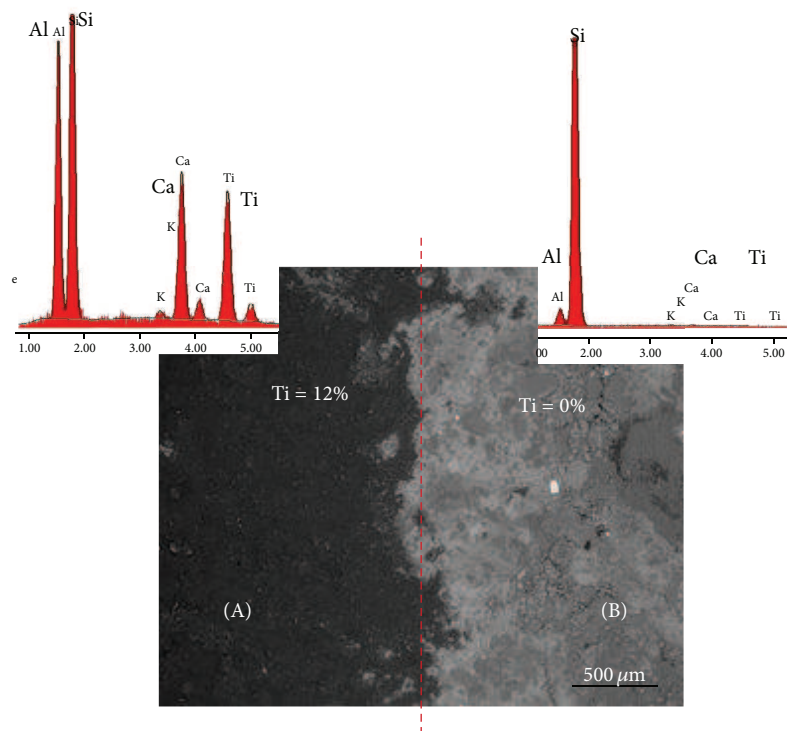


FIGURE 7: SEM image and EDX analysis of the coated and abraded parts of the nanocoating 1 sample; part (A): unabraded coated surface; part (B): abraded.

is supposed to be completely deteriorated during *phase IV* and the brick surface is exposed. The SEM of the brick surface done during this phase (Figure 7) shows a complete absence of Ti.

From these interpretations, since nanocoating 2 does not provide any resistance against abrasion and gets rubbed off easily, it appears that the *phases II* and *III* are totally absent

for nanocoating 2 and uncoated sample and longer *phases I* and *IV* seem to compensate for their absence. The same can be seen in Figures 8(a) and 8(c). If the subscript “0” signifies the uncoated reference, subscript “1” signifies the nanocoating 1 and subscript “2” signifies nanocoating 2, then one can deduce Table 3 where 8 segments (from Figure 8) are represented in the terms of 8 *concentration measures*.

TABLE 3: Representation of segments from Figure 8 in terms of concentration measures.

Segment	AB	BC	EF	FG	GH	HI	KL	LM
Representation	$\left(\frac{\Delta C_0}{\Delta t}\right)_I$	$(C_0)_{IV}$	$\left(\frac{\Delta C_1}{\Delta t}\right)_I$	$(C_1)_{II}$	$\left(\frac{\Delta C_1}{\Delta t}\right)_{III}$	$(C_1)_{IV}$	$\left(\frac{\Delta C_2}{\Delta t}\right)_I$	$(C_2)_{IV}$

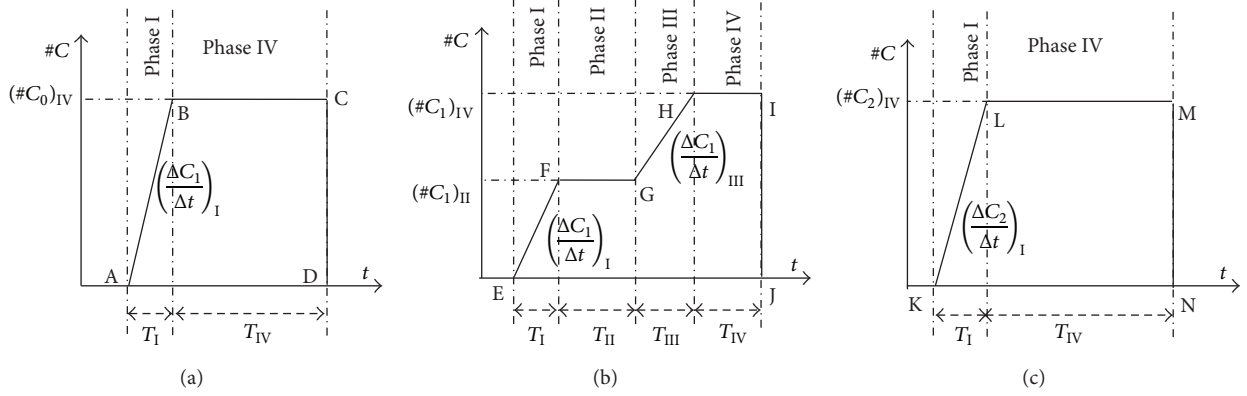


FIGURE 8: Generalized forms of the variation of aerosol particle number concentration generated from (a) uncoated reference (b) nanocoating 1 and (c) nanocoating 2.

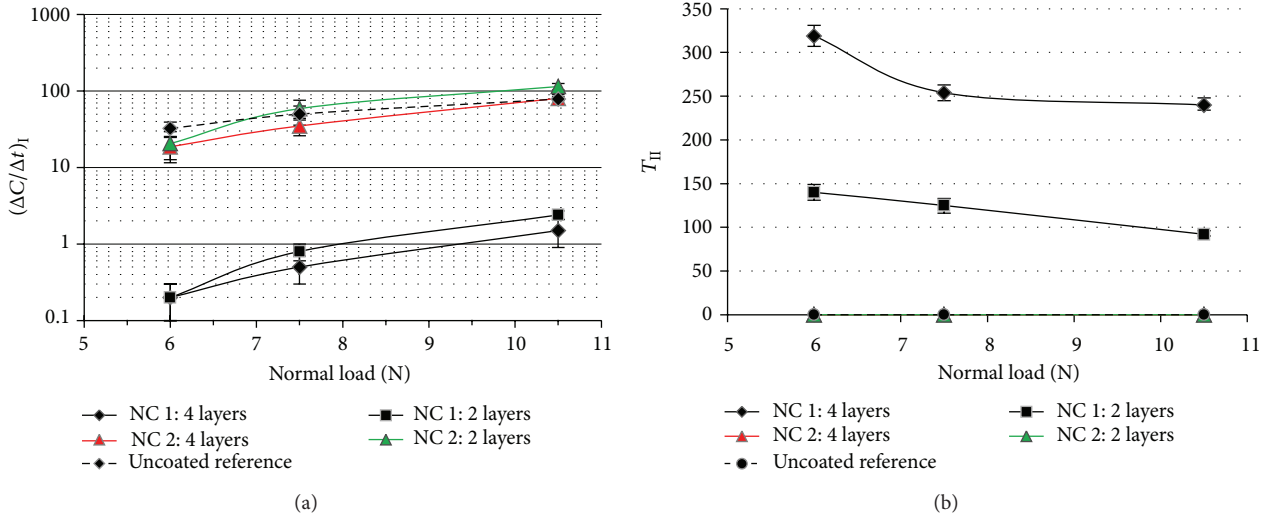


FIGURE 9: (a): Rate of change of the number concentration as a function of the normal load during phase I; (b) phase II duration as a function of the normal load for all nanocoating samples (note: all the curves are mean curves obtained from 3 repeated tests).

In Table 4, the values of these concentration measures are mentioned which were evaluated for all test samples and three normal load values. T_i is the duration of occurrence of the i th phase ($i = I, II, III, IV$). On the basis of this table, it can be said that irrespective of the normal load acting during abrasion, $(\Delta C_0/\Delta t)_I > (\Delta C_1/\Delta t)_I$; $(\Delta C_2/\Delta t)_I > (\Delta C_1/\Delta t)_I$; $(\Delta C_1/\Delta t)_I < (\Delta C_1/\Delta t)_{III}$; $(\#C_0)_{IV} \approx (\#C_1)_{IV} \approx (\#C_2)_{IV}$.

Based on the values obtained in Table 4, rate of change of the number concentration of the released particles during phase I, $(\Delta C/\Delta t)_I$, can be plotted as a function of the normal load for all test samples. This is shown in Figure 9(a). Similarly, the duration of the phase II (T_{II}) can also be plotted as a function of the normal load (see Figures 9(a) and 9(b)).

From these figures, the curves corresponding to the nanocoating 1 (NC 1: 2 layers and NC 1: 4 layers) are clearly distinct from those of the nanocoating 2 (NC 2: 2 layers and NC 2: 4 layers) and the uncoated reference. The nanocoating 1 samples hold the lowest values of $(\Delta C/\Delta t)_I$ with a factor of difference almost equal to 100. This demonstrates their high resistance towards abrasion. At the same time, the nanocoating 1 samples hold the highest values for T_{II} also which demonstrates the highest duration of the stability of the nanocoating 1 during abrasion. This stability increases with the increase in number of nanocoating layers and decreases with the increase in normal load. The nanocoating 2 and the uncoated reference samples have $T_{II} = 0$.

TABLE 4: Values of the concentration measures during the abrasion of all three test samples under all three normal loads (tests repeated thrice).

Test sample	mol	$C(\text{cm}^{-3})$				$\Delta C/\Delta t (\text{cm}^{-3}\text{s}^{-1})$				6 N				10.5 N				7.5 N				10.5 N				
		C_{II}	C_{IV}	C_{II}	C_{IV}	C_{II}	C_{IV}	$\Delta C/\Delta t_{\text{I}}$	$\Delta C/\Delta t_{\text{III}}$	$\Delta C/\Delta t_{\text{I}}$	$\Delta C/\Delta t_{\text{III}}$	T_{I} (s)	T_{II} (s)	T_{IV} (s)	T_{III} (s)	T_{I} (s)	T_{II} (s)	T_{IV} (s)	T_{III} (s)	T_{I} (s)	T_{II} (s)	T_{IV} (s)	T_{III} (s)			
Nano coating	2	20 ± 9	189 ± 6	62 ± 15	372 ± 13	91 ± 17	14	603 ± 14	0.2 ± 0.1	0.9 ± 0.3	0.8 ± 0.2	2.3 ± 0.9	2.4 ± 0.3	4.2 ± 0.4	100 ± 13	140 ± 18	200 ± 14	160 ± 13	62 ± 19	125 ± 17	134 ± 15	279 ± 22	39 ± 14	92 ± 6	120 ± 21	349 ± 12
	4	11 ± 1	196 ± 13	25 ± 8	354 ± 17	43 ± 6	22	618 ± 22	0.2 ± 0.1	0.8 ± 0.5	0.5 ± 0.2	2.2 ± 0.7	1.5 ± 0.6	4 ± 0.8	50 ± 11	319 ± 23	166 ± 16	65 ± 8	42 ± 9	254 ± 19	163 ± 31	141 ± 27	28 ± 12	240 ± 15	147 ± 26	185 ± 12
Nano coating	2	—	172 ± 19	—	347 ± 32	—	34	573 ± 34	20.6 ± 19	—	59 ± 17	—	114.7 ± 11	—	8 ± 5	—	—	592 ± 5	6 ± 5	—	—	592 ± 5	5 ± 4	—	—	595 ± 4
Uncoated	2	—	200 ± 9	—	360 ± 15	—	15	640 ± 15	18.7 ± 6	—	35 ± 9	—	80.4 ± 5	—	11 ± 4	—	—	589 ± 4	10 ± 5	—	—	590 ± 5	8 ± 5	—	—	587 ± 5
Uncoated	—	192 ± 42	—	348 ± 36	—	48	552 ± 48	32.5 ± 7	—	50 ± 4	—	78.7 ± 12	—	6 ± 3	—	—	594 ± 3	5 ± 4	—	—	595 ± 4	7 ± 2	—	—	592 ± 2	

Therefore, the two quantities— $(\Delta C/\Delta t)_I$ and T_{II} —can be used as the *indicators* for the measurement of the particle release tendency of a nanocoating subjected to the abrasion. A more stable (i.e., high T_{II}) and lesser deterioration prone (i.e., low $(\Delta C/\Delta t)_I$) nanocoating yields lesser particle release. The T_{II} can be as high as the duration of the stress application (319 s in the present case) and $(\Delta C/\Delta t)_I$ can be as low as 0 ($0.2 \text{ cm}^{-3} \text{ s}^{-1}$ in the present case).

5. Conclusion

This study has investigated the possibility of the release of aerosol nanoparticles from two commercially available TiO_2 photocatalytic nanocoatings under mechanical stress conditions, simulated using an abrasion process.

The 4 layered nanocoating 1 sample has performed best in inhibiting the particle release, followed by the 2 layered one. However, the nanocoating 2 has not succeeded at all in its inhibition (Figures 3, 5, and 6).

The chemical analysis of the released aerosol particles has shown that, owing to a fast deterioration of the nanocoating 2, the particles were essentially contributed by the brick rather than the nanocoating 2 during abrasion. But in the case of nanocoating 1, it is the other way around.

No free nanoparticles of TiO_2 were found to be present among the released aerosol.

Four different phases during the particle release have been identified and evaluated for all three test samples (Figure 8, Tables 3 and 4).

The two particle release indicators— $(\Delta C/\Delta t)_I$ and T_{IV} —have been introduced which can be used for measuring the holding strength or particle release tendency of a nanocoating (Figure 9).

Further tests shall be done with other nanocoating samples and normal load values to develop a standard test procedure for measuring $(\Delta C/\Delta t)_I$ and T_{IV} . These tests shall be accompanied by other analytical tests too to further strengthen the support for the complete physical interpretations of the four phases.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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References

- [1] M. Stamate and G. Lazar, "Application of titanium dioxide photocatalysis to create self-cleaning materials," *Romanian Technical Sciences Academy MOCM*, vol. 13, no. 3, pp. 280–285, 2007.
- [2] A. Fujishima, K. Hashimoto, and T. Watanabe, *TiO₂ Photocatalysis: Fundamentals and Applications*, BKC, Tokyo, Japan, 1st edition, 1999.
- [3] F. P. Torgal and S. Jalali, "Eco-efficient construction and building materials," *Construction and Building Materials*, vol. 25, no. 2, pp. 582–590, 2011.
- [4] M. Vorbau, L. Hillemann, and M. Stintz, "Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings," *Journal of Aerosol Science*, vol. 40, no. 3, pp. 209–217, 2009.
- [5] S. Suzuki and E. Ando, "Abrasion of thin films deposited onto glass by the Taber test," *Thin Solid Films*, vol. 340, no. 1, pp. 194–200, 1999.
- [6] N. Shandilya, O. le Bihan, and M. Morgeneyer, "A review on the study of the generation of (nano) particles aerosols during the mechanical solicitation of materials," *Journal of Nanomaterials*, vol. 2014, Article ID 289108, 16 pages, 2014.
- [7] M. M. Hassan, H. Dylla, L. N. Mohammad, and T. Rupnow, "Evaluation of the durability of titanium dioxide photocatalyst coating for concrete pavement," *Construction and Building Materials*, vol. 24, no. 8, pp. 1456–1461, 2010.
- [8] D. Gohler, M. Stintz, L. Hillemann, and M. Vorbau, "Characterization of nanoparticle release from surface coatings by the simulation of a sanding process," *Annals of Occupational Hygiene*, vol. 54, no. 6, pp. 615–624, 2010.
- [9] A. T. Saber, I. K. Koponen, K. A. Jensen et al., "Inflammatory and genotoxic effects of sanding dust generated from nanoparticle-containing paints and lacquers," *Nanotoxicology*, vol. 6, no. 7, pp. 776–788, 2012.
- [10] P. C. Raynor, J. I. Cebula, J. S. Spangenberg, B. A. Olson, J. M. Dasch, and J. B. D'Arcy, "Assessing potential nanoparticle release during nanocomposite shredding using direct-reading instruments," *Journal of Occupational and Environmental Hygiene*, vol. 9, no. 1, pp. 1–13, 2012.
- [11] J. Lee, S. Mahendra, and P. J. J. Alvarez, "Nanomaterials in the construction industry: a review of their applications and environmental health and safety considerations," *ACS Nano*, vol. 4, no. 7, pp. 3580–3590, 2010.
- [12] O. le Bihan, N. Shandilya, L. Gheerardyn, O. Guillon, E. Dore, and M. Morgeneyer, "Investigation of the release of particles from a nanocoated product," *Advances in Nanoparticles*, vol. 2, pp. 39–44, 2013.
- [13] J. Petkovic, B. Zegura, M. Stevanovic et al., "DNA damage and alterations in expression of DNA damage responsive genes induced by TiO_2 nanoparticles in human hepatoma HepG2 cells," *Nanotoxicology*, vol. 5, no. 3, pp. 341–353, 2011.
- [14] J. Unnithan, M. U. Rehman, F. J. Ahmad, and M. Samim, "Aqueous synthesis and concentration-dependent dermal toxicity of TiO_2 nanoparticles in Wistar rats," *Biological Trace Element Research*, vol. 143, no. 3, pp. 1682–1694, 2011.
- [15] D. B. Warheit, W. J. Brock, K. P. Lee, T. R. Webb, and K. L. Reed, "Comparative pulmonary toxicity inhalation and instillation studies with different TiO_2 particle formulations: impact of surface treatments on particle toxicity," *Toxicological Sciences*, vol. 88, no. 2, pp. 514–524, 2005.
- [16] ASTM International, "Standard test method for the abrasion of organic coatings by the Taber abrasant," ASTM D4060, 2007.
- [17] ASTM International, "Standard test methods for dry abrasion mar resistance of high gloss coatings," ASTM D6037, 1996.

- [18] ASTM International, "Standard test method for resistance of transparent plastics to surface abrasion," ASTM D1044, 2008.
- [19] L. Golanski, A. Guiot, M. Pras, M. Malarde, and F. Tardif, "Release-ability of nano fillers from different nanomaterials (toward the acceptability of nanoprodukt)," *Journal of Nanoparticle Research*, vol. 14, article 962, 2012.
- [20] W. Boentoro, A. Pflug, and B. Szyszka, "Scratch resistance analysis of coatings on glass and polycarbonate," *Thin Solid Films*, vol. 517, no. 10, pp. 3121–3125, 2009.
- [21] S. Sepeur, N. Kunze, B. Werner, and H. Schmidt, "UV curable hard coatings on plastics," *Thin Solid Films*, vol. 351, no. 1-2, pp. 216–219, 1999.
- [22] D. Katsamberis, K. Browall, C. Iacovangelo, M. Neumann, and H. Morgner, "Highly durable coatings for automotive polycarbonate glazing," *Progress in Organic Coatings*, vol. 34, no. 1-4, pp. 130–134, 1997.
- [23] A. Wank, B. Wielage, H. Pokhmurska, E. Friesen, and G. Reisel, "Comparison of hardmetal and hard chromium coatings under different tribological conditions," *Surface and Coatings Technology*, vol. 201, no. 5, pp. 1975–1980, 2006.
- [24] C.-Y. Huang and C.-I. Tseng, "The effect of interface modification between POM and PTFE on the properties of POM/PTFE composites," *Journal of Applied Polymer Science*, vol. 78, no. 4, pp. 800–807, 2000.
- [25] N. Shandilya, O. le Bihan, M. Morgeneyer, and Y. M. Chen, "Use of a modified Taber abrasion apparatus for investigating the complete stress state during abrasion and in-process wear particle aerosol generation," *Chemical Engineering Research and Design*. In press.
- [26] M. Morgeneyer, O. Le Bihan, A. Ustache, and O. Aguerre-Chariol, "Experimental study of the aerosolization of fine alumina particles from bulk by a vortex shaker," *Powder Technology*, vol. 246, pp. 583–589, 2013.
- [27] O. Le Bihan, M. Morgeneyer, N. Shandilya, O. A. Chariol, and C. Bressot, *Handbook on Safe Use of Nanomaterials Chapter 7.2: Emission Chambers, A Method for Nanosafety*, Academic Press, San Diego, Calif, USA, 2014.
- [28] B. R'mili, O. le Bihan, C. Dutouquet, O. Aguerre-Chariol, and E. Frejafon, "Particle sampling by TEM grid filtration," *Aerosol Science and Technology*, vol. 47, no. 7, pp. 767–775, 2013.
- [29] <http://www.ecomesure.com/Mini-Particle-Sampler-MPS-p-116-c-8-sc-19.html>.
- [30] G. Oberdörster, E. Oberdörster, and J. Oberdörster, "Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles," *Environmental Health Perspectives*, vol. 113, no. 7, pp. 823–839, 2005.
- [31] I. K. Koponen, K. A. Jensen, and T. Schneider, "Sanding dust from nanoparticle-containing paints: physical characterisation," *Journal of Physics: Conference Series*, vol. 151, no. 1, Article ID 012048, 2009.
- [32] A. T. Zimmer and A. D. Maynard, "Investigation of the aerosols produced by a high-speed, hand-held grinder using various substrates," *Annals of Occupational Hygiene*, vol. 46, no. 8, pp. 663–672, 2002.

5.3 Emission from weathered nanocoatings

In the previous sub sections 5.1 and 5.2, the effects of the sole action of the mechanical stresses on the nanostructured products are shown. In those cases, the only force that could bring alternations in the product formulation and design is the mechanical force that is being applied through abrasion.

Another factor which is widely known in the scientific literature to alternate a product's formulation, especially of polymers, is the environmental weathering [5.3.1]. If the nanocoating is used outdoors, it is often exposed to humidity and sunlight containing UV rays with heat. In such conditions, its environmental weathering is inevitable. The environmental weathering- a phenomenon that may have a strong effect on the changes in the material properties due to its exposure to UV rays, humidity and heat- has an important role to play in deciding the nature and number of the released ENM [5.3.2]. It is, therefore, important to analyze this aspect too.

Such an analysis can be performed inside a special weathering chamber (shown in figure 5.1) which does the accelerated artificial weathering of a test sample using laboratory light sources like UV lamps and water sprays. Exposures in such a chamber are conducted in more controlled conditions than the natural environment and are designed to accelerate the degradation of the material.

In the following article entitled “Emission of Titanium Dioxide Nanoparticles from Building Materials to the Environment by Wear and Weather” this aspect is dealt in details. For this study, one of the previously studied nanocoatings, Photocal Masonry[®], is chosen and subjected to the couple of mechanical stresses and environmental weathering. The emission of the ENM (TiO₂ nanoparticles in this case) in air and leaching in water are studied. An international standard, ISO 16474 (formerly known as ISO 11341) is used as a guiding document to select the conditions of exposure.



Figure 5.1: Atlas Suntest XLS+ weathering chamber

The results shown in this article show a step-wise surface deterioration of the nanocoated samples as a function of the duration of a weathering by UV, temperature and water. This surface deterioration led directly to an increase of the emitted aerosol particles number concentration and the TiO₂ content of the aerosolized wear particles. A considerable presence

of free TiO₂ nanoparticles was also observed in the case of the 7 months weathered nanocoated samples. In case of leaching, no such effects were observed during 7 months of weathering. However, fears still remain on how and in what concentrations the leaching of TiO₂ might occur during prolonged weathering durations. This study also discussed the pertinence of the indicators (presented already in the section 5.2) in the context of weathering. They were found to be significant to quantitatively predict the emitted aerosol particles number concentration and nanocoating useful life by the means of linear extrapolation from shorter weathering durations.

[5.3.1] Allen, N.S.; Edge, M.; Corrales, T.; Childs, A.; Liauw, C.M.; Catalina, F.; Peinado, C.; Minihan, A.; Aldcroft, D. Ageing and stabilisation of filled polymers: an overview. *Polym Degrad Stabil* 1998, 61, 183-199.

[5.3.2] Wohleben, 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 re-lease mechanisms and four nanocomposites. *Small* 2011, 7, 2384-2395.

Emission of Titanium Dioxide Nanoparticles from Building Materials to the Environment by Wear and Weather

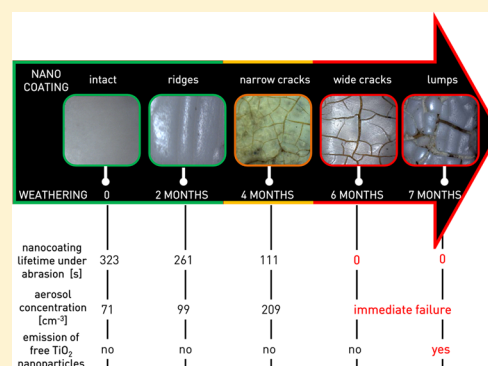
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S Supporting Information

ABSTRACT: In the present work, we investigate the effect of weathering duration on a commercial photocatalytic nanocoating on the basis of its nanoparticle emission tendency into two media, air and water. It is found that increased weathering duration results in stepwise structural deterioration of the nanocoating, which in turn decreases the nanocoating life, changes the nanocoating removal mechanism, and increases the particle emission concentration. Emission of free TiO₂ nanoparticles is found to be weathering duration dependent. Three quantities are introduced: emission transition pace (ETP), stable emission level (SEL), and stable emission duration (SED). By linear extrapolation of these quantities from short weathering durations, complete failure of the nanocoatings can be predicted and, moreover, the potential increase of nanoparticles release into the air.



1. INTRODUCTION

Photocatalytic nanocoatings are readily being applied on the external walls of buildings for their antibacterial and self-cleaning properties.^{1,2} These properties are ensured by the presence of embedded manufactured photocatalytic titanium dioxide (TiO₂) nanoparticles in the coating matrix. Resting on the external surfaces, these nanocoatings are frequently subjected to various mechanical solicitations and environmental weathering in real-life conditions.^{3–5} As a result, the consequent loss of their structural integrity leads to their disintegration, which in turn may lead to exposure of embedded nanoparticles⁶ and thus their possible release too. Depending upon the type of medium in contact, this release can be into air as well as into ground waters. For durable development, understanding their ecological and human health effects is important. In the past decade, slowly though, this concern has started gaining attention.^{6–19} In this context, various toxicological and ecotoxicological studies have also demonstrated toxic effects of some types of TiO₂ nanoparticles.^{20–25}

Here, nanoparticle release from a commercial photocatalytic nanocoating is evaluated as a function of the duration of its weathering. While nanoparticle emission into air is studied via abrasion tests, emission into water is studied via microscopy and leaching tests of runoff samples. Through microscopic studies of the intermediate degraded states of coated surfaces, particle emission is shown to be weathering duration-dependent.

2. MATERIALS AND METHODS

2.1. Samples. For the study, a commercially available photocatalytic nanocoating, Photocal Masonry, was chosen. It is

manufactured by Nanofrance Technologies. It consists of anatase titanium dioxide nanoparticles having a primary size of <8 nm and a volume percentage of 1.1%. Other material properties are as follows: coagulation index, ~2; appearance, white; dispersant, poly(methyl methacrylate) (PMMA). This type of nanocoating is fabricated specifically for applications on porous surfaces like brick, concrete, etc. The substrate chosen for the nanocoating application was a masonry brick (11 cm × 5 cm × 5 cm; Leopard brick, ref 901796, Castorama). It is basically an aluminosilicate brick that is frequently used in constructing façades, house walls, stairs, etc. Microscopic analysis of the nanocoating and the substrate were carried out by optical microscopy (model Imager.M1m, Carl Zeiss MicroImaging GmbH), energy-dispersion spectroscopy (EDS; model X-max, Oxford Instruments), and transmission electron microscopy (TEM; model CM12, Philips). Information on microscopic analysis results is provided in Supporting Information. Four coating layers with a total thickness of ~80 μm were applied on the brick substrates. The substrate surfaces were prepared and the nanocoating was applied following the guidelines in the technical data sheet recommended by the nanocoating manufacturer (i.e., degreased with brush and ethanol-soaked paper, dry and dust-free surfaces; use of a high-volume low-pressure spray during coating; 25 °C ambient temperature).

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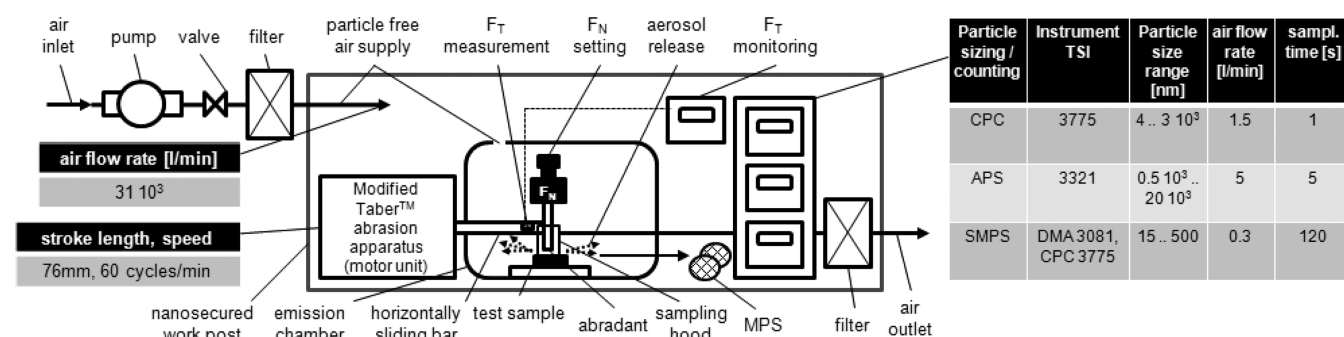


Figure 1. Experimental setup.

2.2. Artificial Weathering. Artificial weathering tests were performed with nanocoated and uncoated reference brick samples in a weathering chamber (model Suntest XLS+, Atlas). Artificial weathering consisted of a maximum of 2658 cycles (which corresponds to 7 months) of 2 h each (120 min of UV light, 102 min dry, 18 min water spray). A xenon arc lamp (300–400 nm; 60 W/m²; model NXE 1700, Ametek SAS) with an optical radiation filter was used as the UV source. Such a system is representative of natural sunlight.²⁰ The temperature during UV exposure was monitored and averaged at 38 °C. Conditions were chosen on the basis of an international standard.²⁶ Deionized and purified water (conductivity <1 μS/cm) was used for water spray onto nanocoated samples. The runoff water was collected in a reservoir, mounted at the bottom of the climate chamber. The whole weathering process was interrupted at selected times (2, 4, 6, and 7 months) for analyzing the in-process condition of the test samples and sampling the collected runoff water for its leaching analysis.

2.3. Leaching. To quantify TiO₂ content in the leachate water, fixed amounts of samples (100 mL) were collected at selected times (as indicated earlier) and analyzed by using inductively coupled plasma mass spectrometry (ICP-MS; model 7500cx, Agilent Technologies). The operating conditions of the ICP-MS were as follows: sample volume, 2 mL; RF power, 1550 W; RF matching, 1.78 V; carrier gas, 0.85 L/min; makeup gas, 0.2 L/min; nebulizer, micromist; nebulizer pump, 0.1 r/s; S/C temperature, 15 °C; He flow rate, 5 mL/min; H₂ flow rate, 2 mL/min; integration time, 0.1 s; chamber and torch, quartz; cone, Ni; element detection threshold limit, 0.5 μg/L.

2.4. Abrasion. A modified Taber linear abrasion apparatus (model 5750, Taber Inc.)²⁷ was used for abrasion of the nanocoated samples. The standard form of this apparatus is referenced in numerous internationally recognized test standards.^{28–30} This apparatus is already being used in industries for analyzing the performance of products like paint, coating, metal, paper, textile, etc., during the application of a mechanical stress.³¹ The normal stress of the abrasant of about 15–500 kPa, being applied through Taber, also corresponds to the typical normal, and thus tangential, stress levels applied to surface coatings in a domestic setting, for example, walking with shoes, displacement of different furnishings, etc.^{3,32} It incorporates a motor-driven horizontal arm (bar) that displaces an abrasant in a back-and-forth linear motion over the test sample. The abrasion is caused by friction at the contact surface between the surfaces of the abrasant and the sample. Via a vertical shaft, a known weight is mounted on the top of the abrasant, which is referred to as the normal load in the following text. Taber H38 nonresilient vitrified clay–carbor-

undum abrasant was used during abrasion of the nanocoated samples. This abrasant comes in a cylindrical shape (6 mm diameter, 2 cm length) and comprises very fine abrasive particles (~4 μm) of carborundum that provide mild abrasion. For reproducing domestic stress conditions, a normal load of 6 N was chosen. An abrasion stroke length of 76 mm, abrasion speed of 60 cycles/min, and abrasion duration of 10 min were other selected parameters.

2.5. Experimental Setup. Figure 1 shows the complete experimental setup. Particle-free air is passed through a nanosecured work post (HPPE 10, Erma Flux S.A., France) containing the Taber abrasion apparatus. Already successfully employed in various nanoparticles' dustiness tests,³³ this work post has a particle filter efficiency of 99.99%. The air flow rate inside this work post is equal to 31 000 L/min. The test sample is placed inside a self-designed emission test chamber (0.5 m × 0.3 m × 0.6 m).³⁴ A small fraction of the air circulating inside the nanosecured work post passes through the emission test chamber before the abrasion tests are started, in order to make the chamber free from background particles. As soon as the chamber becomes particle-free, it is sealed completely. A slot is also provided on one of the walls of this chamber allowing the horizontal arm of the abrasion apparatus to pass through and operate the motor unit placed externally. A radial symmetric sampling hood with a volume of 713 cm³ provides encapsulation of the sampling suction zone around the abrasant. Such a sampling hood has also been employed in other studies with varying volumes, such as 1500 cm³ by Vorbau et al.³ and 60 cm³ by Göhler et al.³⁵ Its use minimizes particle loss to the emission test chamber's walls or other surfaces. Furthermore, the aerosol concentration remains relatively high due to the low volume of the sampling hood and the fixed total sample flow that amounts to 6.8 L/min. The Taber apparatus and the emission test chamber constitute the aerosol generation section (AGS). The AGS is connected to an aerosol measurement section (AMS) by use of antistatic electrically conductive tubes (6 mm diameter), where the generated aerosol particles are characterized in terms of their number concentration and size distribution. The particle number concentration (PNC) can be defined as the number of particles present in a unit centimeter cube of air at a given instant of time. The particle size distribution (PSD) is the classification of the PNC according to size. The instruments used to measure these two quantities were condensation particle counter (CPC), scanning mobility particle sizer (SMPS), aerodynamic particle sizer (APS), and mini particle sampler (MPS; Ecomasure Inc.).³⁶ Details on these instruments and their operation conditions are shown in Figure 1. While the CPC measures the emitted aerosol particles number

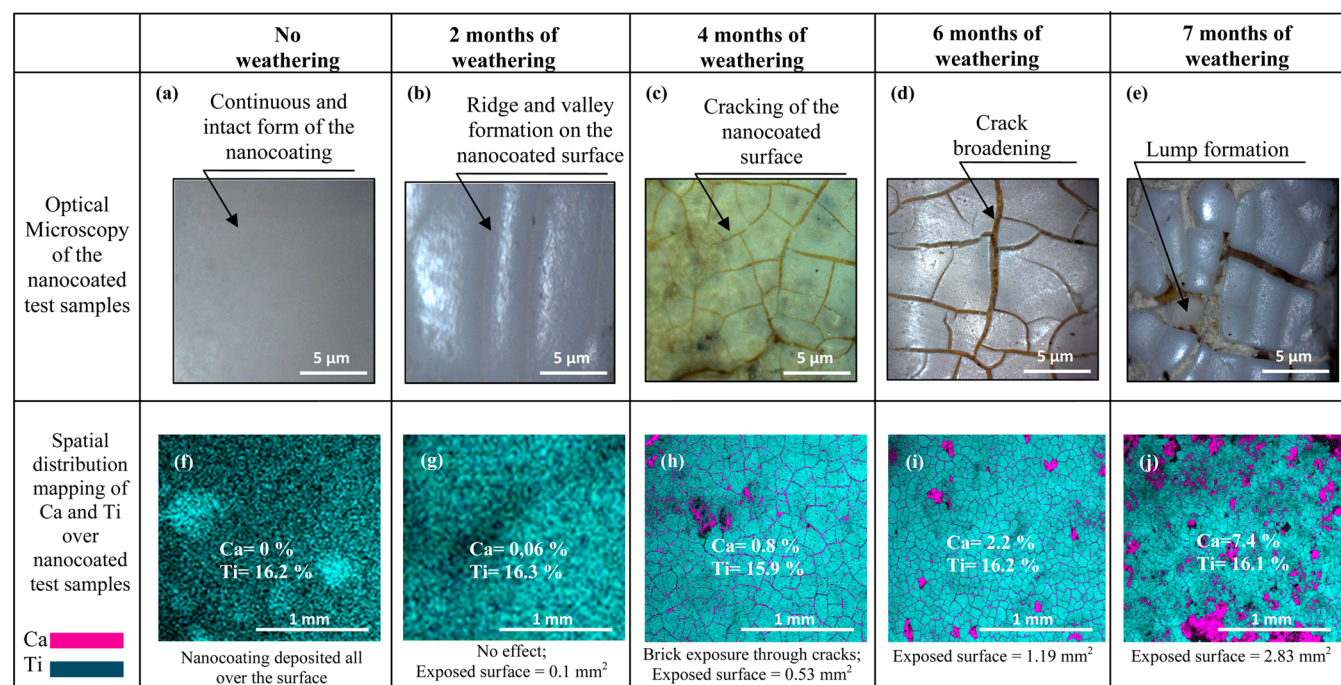


Figure 2. Microscopic analysis of nanocoated sample.

concentration (EAPNC), the PSD is measured by the SMPS and APS. A MPS is used for particle collection through filtration technique on copper mesh grids, which can be used later in TEM for various qualitative analyses of the emitted aerosol particles without any limitation on the aerosol size. Therefore, the whole aerosol measurement section, quantifying the particle emission, can measure aerosol particles having sizes ranging from 4 nm to 20 μm .

2.6. Background and Particle Loss. Three empty test runs were done before the main abrasion experiment to measure the concentration of background particles and those generated by the motor in abrasion apparatus. Without the test sample present in the chamber, the average concentration, detected by CPC within the sampling hood, was $\sim 0.7 \text{ cm}^{-3}$ with a standard deviation of 0.2 cm^{-3} . Therefore, the concentrations of all the background particles and those generated by the abrasion apparatus were insignificant. The calculations on the loss of particle concentration, due to their deposition on the walls of the chamber, have shown a loss of 4% in number during 10 min (i.e., the duration of the abrasion process).

For the present experimental setup, the particle loss in the connecting tubes (i.e., losses due to their gravitational settling, inertial deposition, etc.) has been calculated by Shandilya et al.³⁷ on the basis of a system of equations enlisted by Brockmann.³⁸ Shandilya et al.³⁷ found it to be 17% for particles having size less than or equal to 10 nm. For the 100 nm sized particles or bigger, the loss reduces to a mere 1%.

3. RESULTS AND DISCUSSION

3.1. Structural Deterioration of Nanocoated Sample Surfaces. In Figure 2a–e, the evolution in surface deterioration of the nanocoated sample can be observed with increasing weathering duration. The optical microscopic image of a nonweathered sample (Figure 2a) shows a continuous and intact form. With 2 months of weathering (Figure 2b), ridges and valleys start to appear on the surface. If

the weathering continues, they develop into cracks by 4 months of weathering (Figure 2c). After 6 months, these cracks start to broaden with branching at different parts (Figure 2d). By 7 months, the nanocoating is no longer continuous but reduced in the form of lumps (Figure 2e). On the contrary, for an uncoated reference sample, no such effect of weathering was observed throughout the whole process. In the literature, the cracking of water-based nanocoatings (as in the present case) has been attributed mainly to two factors: drying stress due to water content evaporation^{39–42} and gradual embrittlement of the polymeric binder present in the nanocoating during its interaction with UV rays.⁴³ Moreover, the cracking is often accompanied by shrinking or compaction of the nanocoating on the surface due to the evaporation of water content, as observed by Murray⁴⁰ and Dufresne et al.⁴¹

The nanocoating's shrinking and cracking may result in exposure of the brick surface, lying underneath. In order to confirm this hypothesis, EDS analysis of the weathered nanocoated sample surfaces was done to create an elemental map between Ti (contributed by the nanocoating) and Ca (contributed by the brick). This would show the change in completely exposed surfaces of the brick substrate. The results are shown in Figure 2f–j. One may see that while the Ti content on the surface remains approximately the same throughout the weathering (average value $\sim 16.1\%$), the Ca content and the exposed surface increase proportionately. It directly implies the shrinkage of nanocoating with weathering. If continued further, the increased shrinking may even lead to the increase in Ti percent density in the nanocoating lumps.

3.2. Particle Emission into Water by Leaching. For measuring the emission of TiO_2 nanoparticles in the water, 100 mL aliquots of leachate samples were taken from the collected runoff water at selected times from a reservoir kept beneath the nanocoated samples. For a detection threshold of $0.5 \mu\text{g/L}$ for an element, Ti was found to be always below this threshold in the sample volume, whereas the leached amount of Ca (contributed by the brick) was found to be proportionally

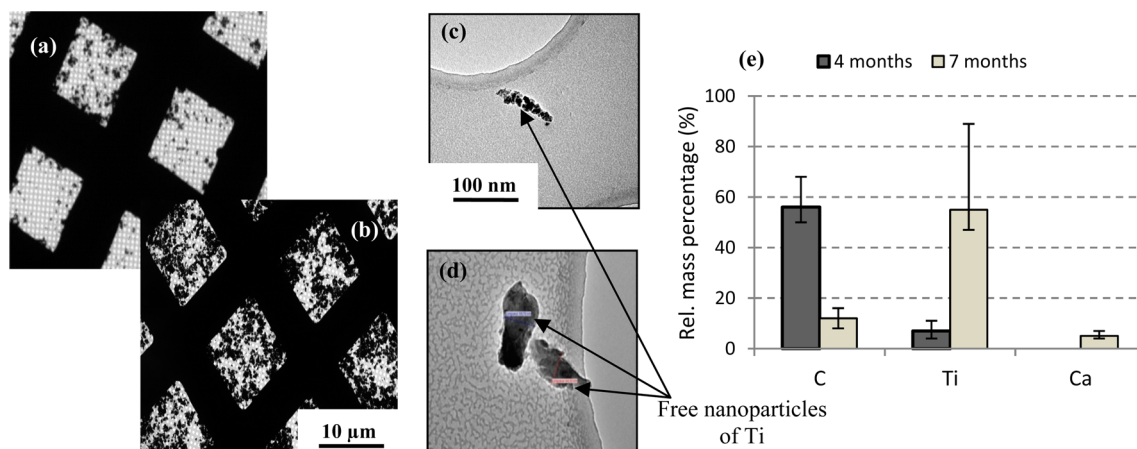


Figure 3. TEM image of aerosol particles emitted from abrasion of (a) 4 months and (b) 7 months weathered nanocoated samples (c, d) Free nanoparticles emitted from abrasion of 7 months weathered nanocoated samples (e) Chemical analysis of aerosol particles emitted from abrasion of 4 and 7 months weathered nanocoated samples.

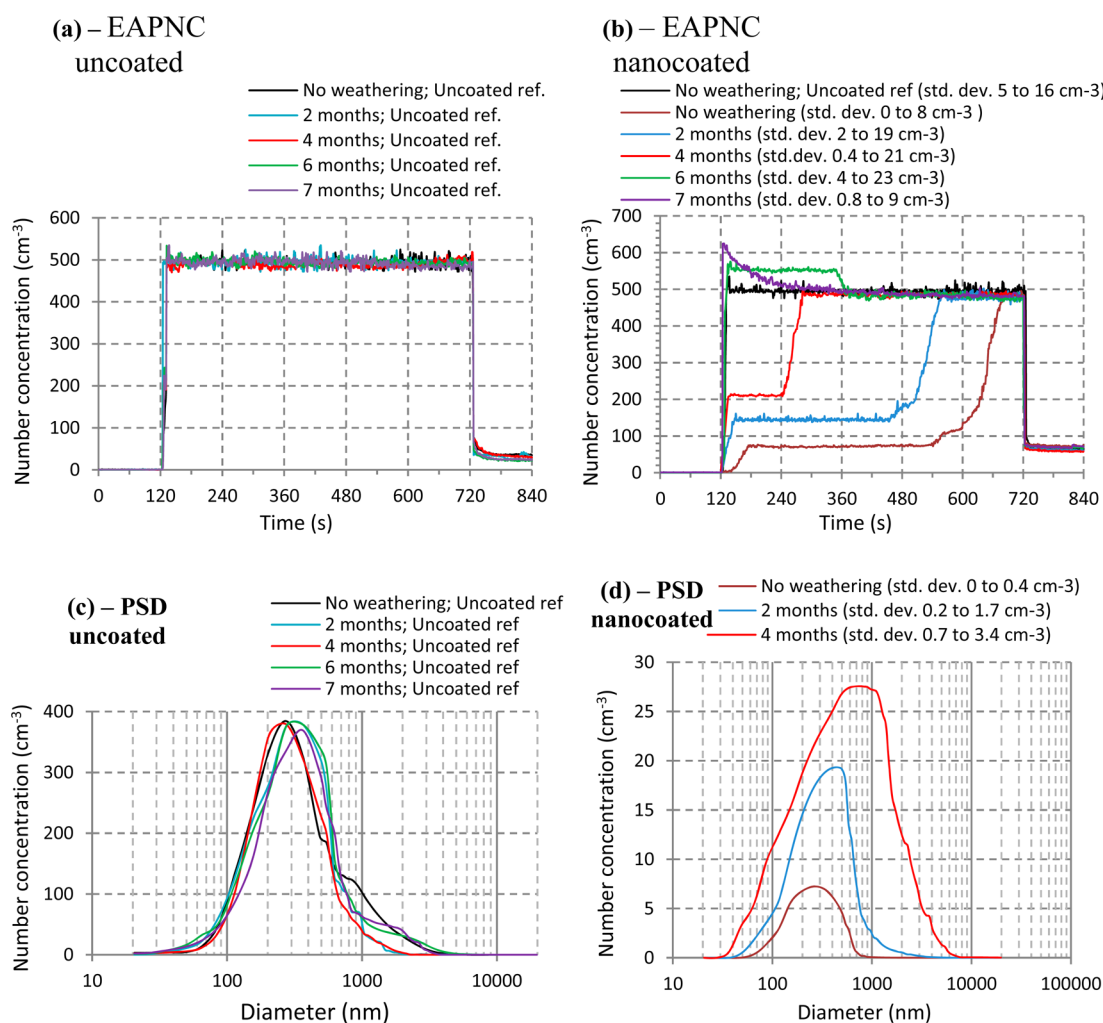


Figure 4. EAPNC and PSD during the abrasion of weathered uncoated and coated samples. The abrasion takes place for $t = 120\text{--}720$ s in panels a and b.

increased with weathering duration. TEM and EDS analysis of various droplets from the leachate samples (test methodology and results described in Supporting Information) showed irregularly shaped micro-sized particle agglomerates.

In coherence with the ICP-MS measurements, EDS analysis of these particle agglomerates also showed an overall increasing Ca content, from 3% to 17% (by mass), with weathering. A meager Ti content (0.2–1% by mass) was observed in all particle agglomerates. The C content (from nanocoating

copolymer) was found to vary from 3% to 10% by mass. The other dominating elements were Si ($\sim 32\%$, by mass) and Al ($\sim 20\%$, by mass). An increased water conductivity (from <1 to $13 \mu\text{S}/\text{cm}$) was also observed in the leachate samples, which is supposed to be a consequence of the increased presence of Si, Al, and Ca.

This concludes that despite the deterioration by weathering, the nanocoated sample surfaces are still strong enough to resist leaching of the constituent nanoparticles into the runoff water. In fact, it is the brick that obviously leaches its constituents into the runoff water. These results seem to be consistent with those of Al-Kattan et al.,¹⁰ who studied the release of Ti, from paints containing TiO_2 nanoparticles, into runoff water under the effect of artificial weathering. They showed a close to background release of Ti, indicating that TiO_2 nanoparticles are strongly bound in the paint.

3.3. Particle Emission into Air by Abrasion. Both uncoated reference and nanocoated samples were abraded after they were exposed to weathering for varying durations. In Figure 3a,b, TEM images are shown of the emitted aerosol particles that were sampled and collected on mesh grids during the first 2 min of abrasion of the 4 and 7 months weathered nanocoated samples under the same sampling conditions. More aerosol particles are deposited on the mesh grids when the weathering duration is increased from 4 to 7 months. Under greater magnification, irregularly shaped polydispersed aerosol particles with no specific evolution in shape, over the variation of the weathering duration, were observed. Most importantly, for 7 months weathered nanocoated samples, the presence of a considerable amount of free nanoparticles of TiO_2 (Ti mass $>90\%$) was observed (Figure 3c,d). Since this result is contrary to the findings of numerous studies,^{4,31,35,44,45} it is of more particular interest, as these studies show that a large fraction of the emitted nanomaterial is present in the matrix-bound form and not in the free state. The increase in relative percent density of Ti, during shrinking of the nanocoating with weathering (as hypothesized earlier) may lead to the generation of these free TiO_2 nanoparticles.

The results on chemical composition of aerosol particles, generated from abrasion of 4 and 7 months weathered nanocoated samples, are shown in Figure 3e. In this figure, the average mass percentages of three elements—C (essentially coming from the nanocoating's copolymer), Ti (essentially coming from the nanocoating), and Ca (essentially coming from the brick)—are shown. One can observe a sharp drop in the relative C content (from 56% to 12%) and a sharp rise in the relative Ti content (from 7% to 55%) when the weathering duration increases from 4 to 7 months. Also, the relative Ca content, which is absent in the case of 4 months weathered nanocoated samples, starts appearing and attains a value of 6% with 7 months of weathering. Hence, a direct impact of weathering duration on the size and chemical composition of the aerosol particles can be observed from these results. Moreover, the chances of exposure of free TiO_2 nanoparticles are much higher in the case of 7 months weathered nanocoated samples.

The results on EAPNC and PSD, measured within the volume of the sampling hood, are shown in Figure 4. In Figure 4a,b, the abrasion test starts at $t = 120$ s and ends at $t = 720$ s. Before and after this time interval (i.e., $t = 0$ – 120 s and $t = 720$ – 840 s), the abrasion apparatus is at rest. For the uncoated reference samples, a constant EAPNC ($\sim 500 \text{ cm}^{-3}$; standard deviation 5 – 16 cm^{-3} ; repeated thrice) is observed, regardless

the weathering duration. Hence, the artificial weathering has no apparent effect on emitted aerosol particles from the uncoated reference sample. However, for the nanocoated samples, EAPNC increases with weathering duration. Except for 6 and 7 months, the nature of its variation with time is also strikingly similar: it ascends initially, becomes constant, ascends again, and becomes constant at last (the PSD, during the first constant phase, is shown in Figure 4d).

For 6 and 7 months weathered nanocoated samples, we observe a rise in the EAPNC curves during their initial phases ($t = 120$ – 360 s) beyond the maximum level observed for the shorter weathering durations. After $t = 360$ s, these curves tend back to the same level as that of the uncoated reference and their counterparts. Such behavior can be explained on the basis of the nanocoating removal mechanism during abrasion of the weathered nanocoated samples. In the case of nonweathered and 2 and 4 months weathered nanocoated samples, the dominant material removal mechanism is assumed to be abrasion wear of the nanocoating due to its continuous and stable form. But for 6 and 7 months weathered nanocoated samples, it is hypothesized that the dominant material removal is rather uprooting of the nanocoating lumps (or soon to be lumps) by the abradant. Since these lumps are loosely attached to the surface, their uprooting is faster and easier. As a result, the EAPNC reaches its highest level as soon as the abrasion starts and comes back to the same level, later, as that of the uncoated reference, when all the nanocoating lumps have been uprooted and the brick surface is completely exposed. The PSD, shown in Figure 4 panels c and d for uncoated reference and nanocoated samples, respectively, varies in a different manner for each sample. While for the uncoated reference samples there is no significant change in the size mode (alternating between 250 and 350 nm) and maximum PNC (lying around 375 cm^{-3} , standard deviation 0.2 – 8 cm^{-3}), continuous evolution can be observed for these two parameters in the case of nanocoated samples.

Coming back to the nature of the EAPNC variation with time, as observed in Figure 4b, an analytic model had been presented by Shandilya et al.⁴⁴ that approximates such a variation in terms of four phases for the present nanocoating and one other commercial one: Tipe E502, TitanPE Technologies, Inc. (see Figure 5). When an uncoated reference

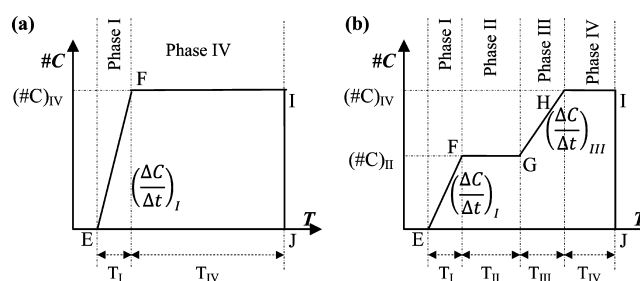


Figure 5. Variation of aerosol particle number concentration generated from (a) uncoated and (b) nanocoated surface samples.

sample is abraded (Figure 4a), the EAPNC reaches a maximum limit swiftly (represented by segment EF in Figure 5a, named as phase I) and then remains constant until the end of the abrasion (represented by segment FI in Figure 5a, named as phase IV). However, the EAPNC, in case of a nanocoated sample (Figure 4b), passes through two intermediate phases (represented by segments FG and GH in Figure 5b; named as

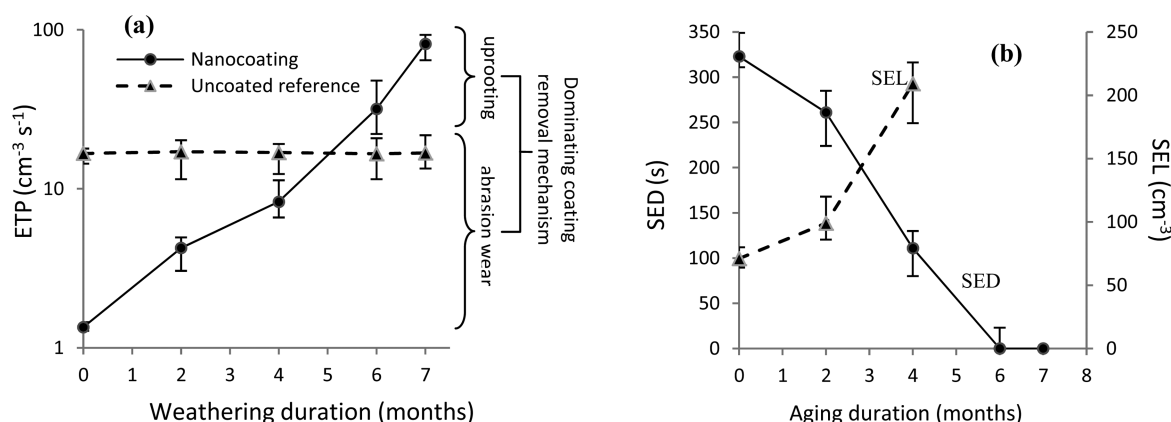


Figure 6. Variation of (a) ETP and (b) SED and SEL with weathering duration.

phases II and III, respectively) before becoming constant at the end, that is, phase IV. Obviously, for an uncoated surface, phases II and III are absent in the evolution of the EAPNC.

If physically interpreted, the phase I is contributed by evolution of the contact surface conditions between abradant and nanocoated sample surface when the abrasion starts. During this phase, an ascending EAPNC is observed. In phase II, the EAPNC is constant and abrasion of the nanocoated sample surface takes place under a stable state. The nanocoating is removed gradually or slowly through its abrasion wear. The duration of this phase also signifies the apparent nanocoating life. By the end of phase II, the surface nanocoating layer is no longer stable and just the nanocoating–brick interface is left. With the advent of phase III, the brick surface starts to become exposed gradually, and by the end of this phase it is completely exposed. Therefore, the EAPNC, during phase IV, arrives at the same level as that of an uncoated reference sample and remains constant afterward.

Three quantities can also be identified from Figure 5 and are discussed in the following: ETP or emission transition pace, $(\Delta C/\Delta t)_i$; SEL or stable emission level, C_{II} ; and SED or stable emission duration, T_{II} . These are important indicators for assessing the nanocoating useful life and EAPNC. In Figure 6, they are plotted as a function of weathering duration. In Figure 6a, we see that ETP (defined as the rate of change of EAPNC) increases with weathering duration for weathered nanocoated samples, whereas for the uncoated reference it remains constant. Moreover, ETP values for nonweathered and 2 and 4 months weathered nanocoated samples lie beneath the level of uncoated reference sample, but for 6 and 7 months weathered nanocoated samples, they lie above this level. On the basis of Figures 2 and 4, we have already hypothesized a change in the nanocoating removal mechanism during the transition of the weathering duration from 4 to 6 months. Therefore, one may conclude that if the ETP value of the EAPNC, from a nanocoated sample, lies beneath the value corresponding to its uncoated reference substrate, the nanocoating removal mechanism is dominated by abrasion wear. If opposite, the uprooting of the nanocoating is more dominant. Under given abrasion conditions, if ETP does not increase with the weathering duration (as observed in the case of uncoated reference), it implies no change in the abrasion conditions, regardless of weathering duration. But if it increases (as observed in the case of weathered nanocoated samples), it implies a change in abrasion conditions. In the present case,

such a change is imparted by deterioration of the nanocoating, as shown, qualitatively, in Figure 2.

The second quantity, SED, is a direct indicator of nanocoating life: the higher the SED, the higher the nanocoating lifetime. It appears to decrease with weathering duration (Figure 6b). When SED = 0, it means that the nanocoating disappears as soon as abrasion starts. Quantitatively, it allows us to extrapolate the effect of shorter weathering durations to longer ones without prolonging the weathering test in reality. In Figure 6b, if the SED average values from the first 2 months of weathering are extrapolated, we observe that SED is reduced to 0 in 11 months. Extrapolation of the extreme limits (i.e., through maximum value of SED for 0 months and minimum value of SED for 2 months) can be used to calculate the minimum useful life of the nanocoating under present weathering conditions. In the present case, we observe that SED is reduced to 0 in 6 months; this is exactly what we observe in Figure 6b. Moreover, the average value of SED decreases from 320 to 110 s (i.e., a reduction factor of ~3) in the mere first 4 months of weathering. The EAPNC during SED is equal to SEL. In Figure 6b, it appears to increase with weathering duration. Since SED = 0 for 6 and 7 months of weathering, therefore, SEL value for these durations cannot be calculated.

In summary, we can say that, under the present experimental conditions, a stepwise and complete surface deterioration of the nanocoated samples was observed as a function of duration of weathering by UV, temperature, and water. This surface deterioration led directly to an increase in the EAPNC (measured within the volume of the sampling hood) and the TiO₂ content of the aerosolized wear particles. A considerable presence of free TiO₂ nanoparticles was observed in the case of the 7 months weathered nanocoated samples. This was a fundamental change observed in the chemical composition of the aerosol particles, as for short weathering durations, TiO₂ nanoparticles were always found to be embedded inside the released coarse wear particles with a polymeric matrix. This increase might still continue for longer weathering durations. With a high specific surface area, these free nanoparticles aerosols now accentuate a potential risk in terms of nanotoxicity. In the case of leaching, no such effects were observed during 7 months of weathering. However, fears still remain about how and in what concentrations the leaching of TiO₂ might occur during prolonged weathering durations. This study also proposed an outline to understand the phenomenon of aerosolization and indicators, such as emission transition

pace, stable emission level, and stable emission duration, for its monitoring. They were found to be significant to quantitatively predict the emitted aerosol particle number concentration and nanocoating useful life by means of linear extrapolation from shorter weathering durations. It is possible to extend this study to a broad spectrum of nanocoatings, with the prospect of seeking their optimal formulations on the basis of nano risk, that is, emissions control.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional text and three figures, describing microscopic analysis of nanocoating solution, uncoated brick, and Taber H38 abrasant; microscopic analysis of leachate water; effect of weathering on uncoated brick reference; and drop deposition technique. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Torgal, F. P.; Jalali, S. Eco-efficient construction and building materials. *Constr. Build. Mater.* **2011**, *25*, 582–590.
- (2) Stamate, M.; Lazar, G. Application of titanium dioxide photocatalysis to create self-cleaning materials. *Modell. Otpim. Mach. Build. Field (MOCM)* **2007**, *13* (3), 280–285.
- (3) Vorbau, M.; Hillemann, L.; Stintz, M. Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings. *Aerosol Sci.* **2009**, *40*, 209–217.
- (4) Shandilya, N.; Le Bihan, O.; Morgeneyer, M. A review on the study of the generation of (nano-) particles aerosols during the mechanical solicitation of materials. *J. Nanomater.* **2014**, No. 289108.
- (5) Le Bihan, O.; Shandilya, N.; Gheerardyn, L.; Guillon, O.; Dore, E.; Morgeneyer, M. Investigation of the Release of Particles from a Nanocoated Product. *Adv. Nanopart.* **2013**, *2*, 39–44.
- (6) Göhler, D.; Nogowski, A.; Fiala, P.; Stintz, M. Nanoparticle release from nanocomposites due to mechanical treatment at two stages of the life-cycle. *J. Phys. Conf. Ser.* **2013**, *429*, No. 012045, DOI: 10.1088/1742-6596/429/1/012045.
- (7) Allen, N. S.; Edge, M.; Corrales, T.; Childs, A.; Liauw, C. M.; Catalina, F.; Peinado, C.; Minihi, A.; Aldcroft, D. Ageing and stabilisation of filled polymers: An overview. *Polym. Degrad. Stab.* **1998**, *61*, 183–199.
- (8) Allen, N. S.; Edge, M.; Ortega, A.; Sandoval, G.; Liauw, C. M.; Verran, J.; Stratton, J.; McIntyre, R. B. Degradation and stabilisation of polymers and coatings: Nano versus pigmentary titania particles. *Polym. Degrad. Stab.* **2004**, *85*, 927–946.
- (9) Hsu, L. Y.; Chein, H. M. Evaluation of nanoparticle emission for TiO₂ nanopowder coating materials. *J. Nanopart. Res.* **2007**, *9*, 157–163.
- (10) Al-Kattan, A.; Wichser, A.; Vonbank, R.; Brunner, S.; Ulrich, A.; Zuind, S.; Nowack, B. Release of TiO₂ from paints containing pigment-TiO₂ or nano-TiO₂ by weathering. *Environ. Sci. Process Impact* **2013**, *15*, 2186–2193.
- (11) Kaegi, R.; Ulrich, A.; Sinnet, B.; Vonbank, R.; Wichser, A.; Zuleeg, S.; Simmler, H.; Brunner, S.; Vonmont, H.; Burkhardt, M.; Boller, M. Synthetic TiO₂ nanoparticle emission from exterior facades into the aquatic environment. *Environ. Pollut.* **2008**, *156*, 233–239.
- (12) Hirth, S.; Cena, L.; Cox, G.; Tomovic, Z.; Peters, T.; Wohlleben, W. Scenarios and methods that induce protruding or released CNTs after degradation of nanocomposite materials. *J. Nanopart. Res.* **2013**, *15*, 1504–1518.
- (13) 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**, *7*, 2384–2395.
- (14) Al-Kattan, A.; Wichser, A.; Zuin, S.; Arroyo, Y.; Golanski, L.; Ulrich, A.; Nowack, B. Behavior of TiO₂ released from nano-TiO₂-containing paint and comparison to pristine nano-TiO₂. *Environ. Sci. Technol.* **2014**, *48*, 6710–6718.
- (15) Gondikas, A. P.; von der Kammer, F.; Reed, R. B.; Wagner, S.; Ranville, J. F.; Hofmann, T. Release of TiO₂ nanoparticles from sunscreens into surface waters: A one-year survey at the old danube recreational lake. *Environ. Sci. Technol.* **2014**, *48*, 5415–5422.
- (16) von Goetz, N.; Lorenz, C.; Windler, L.; Nowack, B.; Heuberger, M.; Hungerbühler, K. Migration of Ag- and TiO₂- (nano)particles from textiles into artificial sweat under physical stress: experiments and exposure modeling. *Environ. Sci. Technol.* **2013**, *47*, 9979–9987.
- (17) Windler, L.; Lorenz, C.; von Goetz, N.; Hungerbühler, K.; Amberg, M.; Heuberger, M.; Nowack, B. Release of titanium dioxide from textiles during washing. *Environ. Sci. Technol.* **2012**, *46*, 8181–8188.
- (18) Zhang, W.; Crittenden, J.; Li, K. G.; Chen, Y. S. Attachment efficiency of nanoparticle aggregation in aqueous dispersions: Modeling and experimental validation. *Environ. Sci. Technol.* **2012**, *46*, 7054–7062.
- (19) Stefano, Z.; Marco, G.; Arlen, F.; Luan, G. Leaching of nanoparticles from experimental water-borne paints under laboratory test conditions. *J. Nanopart. Res.* **2013**, *16*, 2185.
- (20) Petkovic, J.; Zegura, B.; Stevanovic, M.; Drnovsek, N.; Uskokovic, D.; Novak, S. DNA damage and alterations in expression of DNA damage responsive genes induced by TiO₂ nanoparticles in human hepatoma HepG2 cells. *Nanotoxicology* **2011**, *5*, 341–353.
- (21) Unnithan, J.; Rehman, M. U.; Ahmad, F. J.; Samim, M. Aqueous synthesis and concentration-dependent dermal toxicity of TiO₂ nanoparticles in wistar rats. *Biol. Trace Elem. Res.* **2011**, *143*, 1682–1694.
- (22) Warheit, D. B.; Brock, W. J.; Lee, K. P.; Webb, T. R.; Reed, K. L. Comparative pulmonary toxicity inhalation and instillation studies with different TiO₂ particle formulations. *Toxicol. Sci.* **2005**, *88*, 514–524.
- (23) Yamashita, K.; Yoshioka, Y.; Higashisaka, K.; Mimura, K.; Morishita, Y.; Nozaki, M.; Yoshida, T.; Ogura, T.; Nabeshi, H.; Nagano, K.; Abe, Y.; Kamada, H.; Monobe, Y.; Imazawa, T.; Aoshima, H.; Shishido, K.; Kawai, Y.; Mayumi, T.; Tsunoda, S.; Itoh, N.; Yoshikawa, T.; Yanagihara, I.; Saito, S.; Tsutsumi, Y. Silica and titanium dioxide nanoparticles cause pregnancy complications in mice. *Nat. Nanotechnol.* **2011**, *6*, 321–328.
- (24) Barnard, A. S. One-to-one comparison of sunscreen efficacy, aesthetics and potential nanotoxicity. *Nat. Nanotechnol.* **2010**, *5*, 271–274.
- (25) Auffan, M.; Rose, J.; Bottero, J. Y.; Lowry, G. V.; Jolivet, J. P.; Wiesner, M. R. Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective. *Nat. Nanotechnol.* **2009**, *4*, 634–641.

- (26) AFNOR. Paints and varnishes – Methods of exposure to laboratory light sources – Part 1: General guidance; ISO 16474-1; 2012.
- (27) Morgeneyer, M.; Shandilya, N.; Chen, Y. M.; Le Bihan, O. Use of a modified Taber abrasion apparatus for investigating the complete stress state during abrasion and in-process wear particle aerosol generation. *Chem. Eng. Res. Des.* **2015**, *93*, 251–256.
- (28) ASTM International. Standard test method for the abrasion of organic coatings by the Taber Abradant; ASTM D 4060; 2007.
- (29) ASTM International. Standard test method for dry abrasion mar resistance of high gloss coatings; ASTM D 6037; 1996.
- (30) ASTM International. Standard test method for resistance of transparent plastics to surface abrasion; ASTM D 1044; 2008.
- (31) Golanski, L.; Guiot, A.; Pras, M.; Malarde, M.; Tardif, F. Release-ability of nano fillers from different nanomaterials (toward the acceptability of nanoproduct). *J. Nanopart. Res.* **2012**, *14*, 962–970.
- (32) Hassan, M. M.; Dylla, H.; Mohammad, L. N.; Rupnow, T. Evaluation of the durability of titanium dioxide photocatalyst coating for concrete pavement. *Constr. Build. Mater.* **2010**, *24*, 1456–1461.
- (33) Morgeneyer, M.; Le Bihan, O.; Ustache, A.; Aguerre Chariol, O. Experimental study of the aerosolization of fine alumina particles from bulk by a vortex shaker. *Powder Technol.* **2013**, *246*, 583–589.
- (34) Le Bihan, O.; Morgeneyer, M.; Shandilya, N.; Aguerre Chariol, O.; Bressot, C. In *Handbook of Nanosafety: Measurement, Exposure and Toxicology*; Vogel, U., Savolainen, K., Wu, Q., Van Tongeren, M., Brouwer, D., Berges, M., Eds.; Academic Press: San Diego, CA, 2014; Chapt. 7.
- (35) 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.* **2010**, *54*, 615–624.
- (36) R'mili, B.; Le Bihan, O.; Dutouquet, C.; Aguerre Charriol, O.; Frejafon, E. Sampling by TEM grid filtration. *Aerosol Sci. Technol.* **2013**, *47*, 767–775.
- (37) Shandilya, N.; Le Bihan, O.; Morgeneyer, M. Effect of the normal load on the release of aerosol wear particles during abrasion. *Tribol. Lett.* **2014**, *55*, 227–234.
- (38) Brockmann, J. E. In *Aerosol Measurement: Principles, Techniques and Applications*; Kulkarni, P., Baron, P. A., Willeke, K., Eds.; John Wiley & Sons: Hoboken, NJ, 2011; Chapt. 6.
- (39) White, L. R. Capillary rise in powders. *J. Colloid Interface Sci.* **1982**, *90*, 536–538.
- (40) Murray, M. Cracking in coatings from colloidal dispersions: An industrial perspective. Proceedings Rideal Lecture, London, April 20, 2009.
- (41) Dufresne, E. R.; Corwin, E. I.; Greenblatt, N. A.; Ashmore, J.; Wang, D. Y.; Dinsmore, A. D.; Cheng, J. X.; Xie, X. S.; Hutchinson, J. W.; Weitz, D. A. Flow and fracture in drying nanoparticle suspensions. *Phys. Rev. Lett.* **2003**, *91*, No. 224501.
- (42) Tirumkudulu, M. S.; Russel, W. B. Cracking in drying latex films. *Langmuir* **2005**, *21*, 4938–4948.
- (43) Hare, C. H. The degradation of coatings by ultraviolet light and electromagnetic radiation. *J. Prot. Coat. Linings* **1992** (May).
- (44) Shandilya, N.; Le Bihan, O.; Bressot, C.; Morgeneyer, M. Evaluation of the particle aerosolization from n-TiO₂ photocatalytic nanocoatings under abrasion. *J. Nanomater.* **2014**, No. 185080.
- (45) Tomasetta, I.; Barletta, D.; Lettieri, P.; Poletto, M. The measurement of powder flow properties with a mechanically stirred aerated bed. *Chem. Eng. Sci.* **2012**, *69*, 373–381.

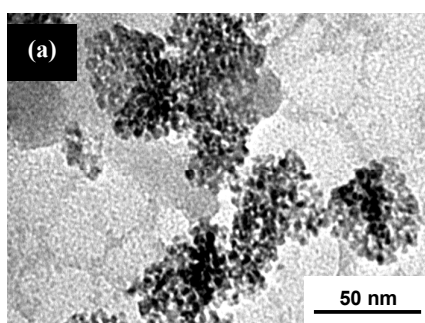
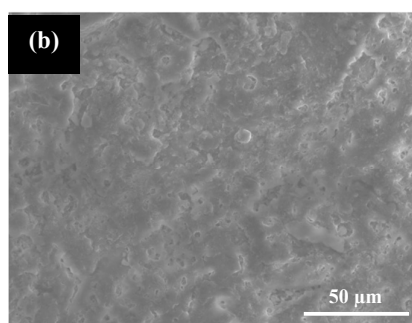
Supporting Information

Emission of Titanium dioxide nanoparticles from building materials to the environment by wear and weather

*Neeraj Shandilya, Olivier Le Bihan, Christophe Bressot, Martin Morgeneyer**

Microscopic analysis of the nanocoating solution, uncoated brick and the Taber™ H38 abradant

TEM analysis of the nanocoating solution was carried out using drop deposition technique (described in the section 2). The result is shown in figure 1 (a). The two phase agglomerates of the deposited particles from the nanocoating can be observed. These two phases are contributed by the polymer matrix (in grey color) and incorporated TiO₂ nanoparticles (in pitch black color). The average TiO₂ particle size is measured to be 8 ± 4 nm. The Energy-dispersive X-ray analysis (EDX; Model X-max; Oxford Instruments UK) of the elemental composition of the nanocoating show the following: C (60 to 65% in mass), O (15 to 20% in mass) and Ti (10 to 15% in mass). In figures 1 (b) and (c), SEM images of the uncoated brick reference and the Taber H38 abradant are shown. Rough surfaces (r.m.s. roughness for brick: 26 μ m; r.m.s. roughness for abradant: 4 μ m) can be observed.



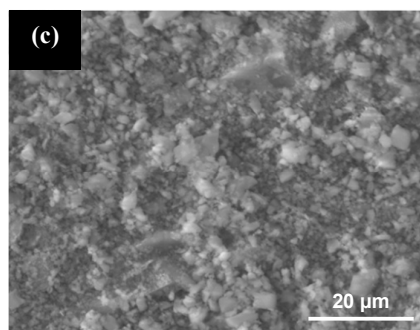


Figure S1. (a) TEM image of the nanoparticles present in the nanocoating (b) SEM image of the uncoated brick surface (c) SEM image of the Taber™ H38 abradant

Microscopic analysis of leachate water

When the leachate water samples were analyzed using TEM, various irregularly shaped particle agglomerates, in micro size ranges, were observed (figure 2 (a) and (b)). In coherence with the ICP-MS measurements, the EDX analysis of these particle agglomerates (figure 2 (c), (d) and (e)) showed an overall increasing Ca content, from 3 to 17% (by mass), with weathering duration. A meager Ti content (0.2-1%, by mass) was observed in all grids. The C content (from nanocoating copolymer) was found to be varying from 3 to 10 % by mass. The other dominating elements were Si (~32%, by mass) and Al (~20%, by mass).

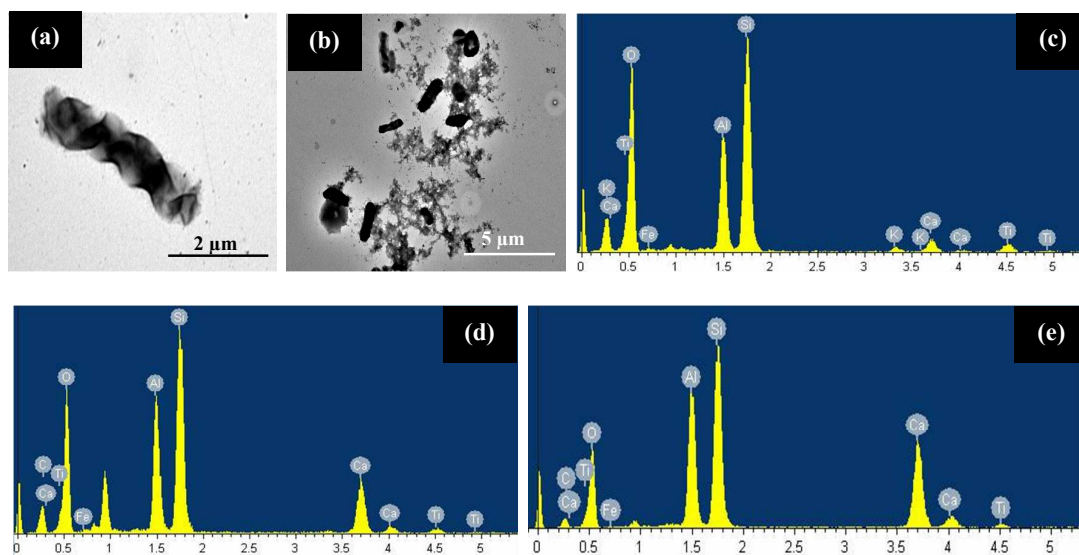
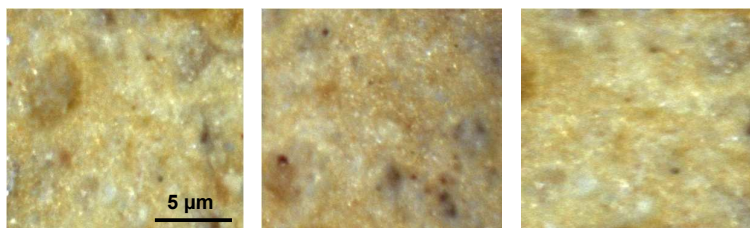


Figure S2. TEM analysis of (a) & (b) Particle agglomerates present in the leachate water sample; Average chemical spectrum of the leachate water sample obtained after (c) 2 months (d) 4 months (e) 7 months of weathering

43 **Effect of weathering on uncoated brick reference**

44 In figure 3, optical microscopic images of 3 different surface spots, on a 7 months weathered
45 uncoated reference sample, are shown. Opposed to the nanocoated surfaces, no effect of
46 weathering (i.e. cracking or lumping) is visible.

47



48

49 **Figure S3.** Optical microscopic images of different spots on the surface of 7 months
50 weathered uncoated reference sample
51

52 **Drop deposition technique**

53 For the TEM analysis, first a diluted solution of the sample was prepared (1% by volume for
54 the nanocoating, no dilution for the leachate sample). A drop (8 μl approx.) from this diluted
55 solution was deposited onto a TEM copper mesh grid (Model S143-3; Quantifoil Micro Tools
56 GmbH Germany). The mesh grid was made hydrophilic by its plasma treatment- 0.1 mbar, 45
57 mA, 3 min- (Model K100X, Glow Discharge, Emitech, Quorum Technologies Ltd. UK) prior
58 to drop deposition. After the deposition, the grid was then allowed to dry in a closed chamber
59 so that the water content gets evaporated and the constituent particles rest deposited on the
60 grid.

5.4 General conclusion from case studies

On the basis of the studies presented in this section, one may infer that if a stress (mechanical or environmental or both) can succeed in dismantling the interfacial adhesion forces, acting between the ENM and the matrix, emission of the ENM aerosols is highly probable. It has been seen that the mechanical stresses alone are not sufficient enough to do so. The aerosol obtained in this case always had ENM embedded inside the product matrix. However, when the environmental weathering is applied in addition, as soon as a certain threshold of the duration is crossed (7 months in the present case), not only the emission is supposed to increase but free ENM may also start to appear in the generated aerosol.

6. EMISSION MODELING

6.1 Introduction

6.1.1 The need and present limitations

As already iterated in the section 1, many studies have shown that when the surface of traditional and nanostructured products are subjected to mechanical stress, aerosolization of wear particles, containing ENM, can occur [6.1-6.4]. Such an aerosol comprises of nano and micro particles which are prone to human interactions, either through their inhalation or dermal contact upon exposure. Various toxicological studies have demonstrated toxic effects of some types of ENM in this case [6.5-6.10] too.

Conventionally, various mechanical solicitation tests like abrasion, drilling etc. are carried out to quantify the tendency of different products towards the generation of nano and microparticles of aerosols. However, these experimental approaches suffer from a limitation due to the aerosol particles loss [6.11] before they are quantified. This loss may occur in different independent scenarios. For example, during their transportation from the aerosol generating source to the characterizing instruments; and deposition of the particles back to the surface from which they generated due to the development of surface electrostatic charges; and deposition on the surrounding walls or intermediate surfaces etc. Therefore, these experimental approaches are rather *semi-quantitative* i.e. they fall short of measuring the final quantitative value of the generated aerosols.

One may account for these losses by using various simplified equations and performing NaCl aerosol surface deposition test, as outlined in the article entitled “Effect of the normal load on the release of aerosol wear particles during abrasion” in the section 5.1 and described in [6.18]. However, the results of these tests completely depend upon the configuration of different elements in the experimental set-up. In other words, a slight change in the diameter, length or angle of orientation of an element like a transporting tube can easily change the total loss in the aerosol particles passing through it easily. Hence, in order to avoid doing the losses calculations each time an experimental test is done, one is obliged to repeat the same experimental set-up configuration. However, performing each test under exactly the same experimental set-up configuration is not feasible as it can get altered by the change in the test sample dimensions.

In one of the review studies [6.2], seeking to present the forefront of this subject, a need to understand and identify various underlying physical phenomena that lead to the emission has also been pointed out that that may help in a more sustainable and durable development of the use of nanotechnology in product design.

6.1.2 The proposed solution

Thus, with an aim to expand our knowledge on the release mechanisms of the aerosol particles and their prediction, an attempt has been made to develop a predictive analytical model. By considering different material and mechanical stress parameters, this model calculates the number of aerosol particles that get generated during the sliding abrasion of a product.

In this model, depending on the product type, the number of the total wear particles, comprising of both aerosol (or airborne) and deposited form of wear debris, is first calculated

by evaluating the total wear volume using Archard law, JKR and DMT theories. Assuming a spherical shape of all the particles, their total number is then evaluated by dividing the total wear volume with the volume of a unit particle. Then, Rosin Rammler or modified Weibull distribution function is used to approximate the size distribution of the wear particles.

Once the number of wear particles and their size distribution are approximated, their aerosolization probability is evaluated by balancing the effect of four principal forces i.e. Gravitation, Diffusion, Drag and Net mechanical input, which act simultaneously on a wear particle. By doing so, an aerosolization criterion can be developed. All those particles which fulfill this criterion aerosolize or get airborne, the others do not.

The number of aerosol particles is then finally calculated by multiplying the number of wear particles with their aerosolization probability.

To validate the model, its results (obtained after curve fitting) are compared with the experimentally obtained ones. These experimentally obtained results have been treated with calculations of the aerosol particles losses before they were compared with the model results. Due to a close agreement between the two, it appears to work well under the present experimental conditions. This is verified for three different materials. The model simulation and a sensitivity analysis of different parameters help in determining the parameters to which the emission of the aerosol particles is most susceptible to.

6.2 Nomenclature

a_i	True radius of contact at i^{th} abrasion stroke[m]	p	Pressure [Pa]
A_c	Total area of contact [m ²]	$P(d_p)$	Aerosolization probability [#]
B	Mechanical mobility [m/N.s]	P_{80}	80 th percentile of the wear particles' diameters range [#]
C_c	Slip correction factor [#]	r_1	rms radius of the sample surface asperities [m]
C_d	Drag coefficient [#]	r_2	rms radius of the abradant surface asperities [m]
d_p	Particle diameter or size [μm]	Re_p	Particle Reynolds number [#]
D	Diffusivity [mm ² /s]	S	Total abrasion distance [m]
E_a	Energy absorbed during fracturing [J]	t	Abrasion duration [min]
E_1	Young's modulus of the sample surface [Pa]	T	Temperature [K]
E_2	Young's modulus of the abradant surface [Pa]	t_{imp}	Abradant-asperity impact duration [μs]
$f(z)$	Asperity height distribution	V	Settling velocity [m/s]
F_d	Drag force [N]	V_w	Total wear volume [m ³]
F_{diff}	Diffusion force [N]	V_{wa}	Aerosolizable wear volume [m ³]
F_{eq}	Force corresponding von Mises stress [N]	V_{wd}	Debris form of the wear volume [m ³]
F_g	Gravitational force [N]	x_c	Critical crack length [m]
F_{in}	Total input force acting on an asperity [N]	Y	A crack form dependent constant [#]
F_{mech}	Total mechanical force acting on a wear particle [N]	z	Variable representing asperity height
F_N	Normal force [N]	z_{max}	Highest asperity height available on the sample surface before the abrasion [m]
$(F_N)_{cr}$	Value of F_N at which the wear volume generation deviates from the Archard law [N]	z_n	Highest asperity height available on the sample surface after the abrasion [m]
F_T	Tangential force [N]	Z_0	Constant accounting for a separation distance between two atoms in equilibrium [#]
F'	Force used to fracture an asperity [N]	α	Surface porosity [#]
g	Acceleration due to gravity [m/s ²]	ρ_g	Air density [kg/m ³]
H	Sample surface hardness [N/m ²]	ρ_p	Particle density [kg/m ³]
k	Boltzmann constant [N.m/K]	η	air viscosity coefficient [Pa.s]
K	Archard wear constant [#]	ν_1	Poisson's ratio of the sample [#]
K_C	Asperity fracture toughness [Pa√m]	ν_2	Poisson's ratio of the abradant [#]
K_I	Stress intensity factor during mode 1 fracturing [Pa√m]	σ	Standard deviation in asperity height distribution [m]
K_2	Stress intensity factor during mode 2 fracturing [Pa√m]	σ_s	Stress acting on the contact area [N/m ²]
l	Notch length [m]	σ_y	Yield stress [N/m ²]
m	Mild or severe abrasion regime describing parameter [#]	Γ	Sample surface energy [J/m ²]
$\max\{F_N\}$	Maximum permissible value of F_N until a macroscopic failure [N]	ψ	Asperity number density [#m ²]
m_p	Particle mass [g]	ω	Plasticity index [#]
n	Number of asperities in contact [#]	$\emptyset$	Scale parameter of the assumed gamma distribution [#]
$N(d_p)$	Number of wear particles [#]	ϵ	Shape parameter of the assumed gamma distribution [#]
$N_{air}(d_p)$	Number of aerosol particles [#]		

6.3 Assumptions

Field of study	Code	Assumption/Hypothesis	Comments
Tribology	T.1	The asperity height distribution on the test sample surface follows a normal distribution	See [6.12-6.14]
	T.2	Each asperity has at most single contact with the abrasant	See [6.15]
	T.3	All microscopic contacts, between abrasant and the sample surface asperities, carry equal load.	See [6.17]
	T.4	The individual contact circle radius of an asperity with the abrasant can be calculated using JKR or DMT criterion.	See [6.16]
	T.5	Particles generated during abrasion have same aerodynamic properties as that of a spherical particle.	See [6.15]
	T.6	Temperature effects at the interface of the abrasant and the test sample are negligible.	For the sake of simplicity; Completely valid for the low abrasion speed and normal force.
	T.7	The wear volume from the abrasant is negligible w.r.t. that of the sample.	The wear volume of the abrasant was always observed experimentally to be less than 2% of the worn volume of the test sample. For ex. see [6.12]
Aerosol physics	A.1	The size distribution of the aerosol particles, generated during abrasion, follows gamma distribution	See [6.18]
	A.2	There are no losses in particle count due to their deposition on walls or other surfaces present inside the emission chamber.	If the particle sampling is being done in the vicinity of the particle generation source, the particles do not get any chance to get deposited on a surface.
	A.3	The effects of the phenomena like thermophoresis, photophoresis, external wave pressures and electrostatic charge deposition on the aerosol particles are negligible.	Under controlled conditions where there are no light, acoustic and thermal pressures, the effects of these phenomena are insignificant.
Material physics	P.1	The size distribution of the all wear particles (debris+aerosols), generated during abrasion, follows Rosin-Rammler distribution.	See [6.19]
	P.2	An asperity failure occurs through its fracturing.	-
	P.3	A part of the input mechanical force, applied through the abrasant, is consumed in the asperity failure and the remaining part of the force acts equally on all wear particles generated after asperity failure.	See [6.20]
	P.4	The pre-existing cracks, present in an asperity, are in the form of vertically aligned notches which intrigue the cracks to pass through them under low normal load or mild abrasion conditions.	Although multiple alignments for the pre-existing cracks in an asperity are possible, a vertical one is chosen for the sake of simplicity.

6.4 Materials and Methods

6.4.1 Test Samples

Three test samples- brick, wood and stainless steel, are chosen for the study. This choice is justified later in the section 6.6.1. In table 6.1, the numerical values of their material properties are shown.

Parameter	Brick	Wood	S. Steel	Parameter	Brick	Wood	S. Steel
E_I	1.5 GPa ^[6.21]	1 GPa ^[6.22]	200 GPa ^[6.23]	ν_I	0.2 ^[6.21]	0.7 ^[6.22]	0.6 ^[6.23]
$(F_N)_{cr}$	12 N*	8 N*	25 N*	Y	1.12 ^[6.25]	1.12 ^[6.25]	1.12 ^[6.25]
F_T	6 N*	(0.488 x F_N)/ t^a N*	3 N*	z_{max}	40 μm^*	40 μm^*	0.7 μm^*
H	800 HV ^[6.21]	520 HV ^[6.24]	1200 HV ^[6.23]	z_n	-10 μm^*	-30 μm^*	0*
K	4.2x10 ⁻⁶ *	0.8*	6.2x10 ⁻⁶ *	ρ_p	1700 kg/m ³ ^[6.26]	860 kg/m ³ ^[6.26]	7850 kg/m ³ ^[6.26]
l	0.01 x r_1 **	0.01 x r_1 **	10 ⁻⁹ x r_1 **	γ	7.2 J/m ² ^[6.27]	16 J/m ² ^[6.27]	0.1 J/m ² ^[6.27]
$\max\{F_N\}$	20 N*	16 N*	37 N*	ψ	5x10 ¹² m ⁻² *	4.75x10 ¹² m ⁻² *	17x10 ¹² m ⁻² *
r_I	7 μm^*	11 μm^*	0.03 μm^*	α	-	0.36**	-

Table 6.1: Numerical values of the material parameters of the test samples (**experimentally measured*; ***proposed values for best fit with the experimental data*)

One may note that the value of F_T for the wood sample is not constant, but a variable that depends on the abrasion duration, t , and the porosity measure, α . Due to a porous nature of the wood surface, there is a continuous evolution in the value of F_T with the abrasion duration. This aspect shall be discussed in more details later.

6.4.2 Abrasion process and Experimental setup

The modified Taber linear abrasion apparatus [6.28] was used for the abrasion of the three test samples. In table 6.2, the numerical values of the abradant materials properties are shown with the conditions in which the abrasion test were carried out. The experimental set-up has already been discussed in the section 4.

A.S.	t	E_2	k	p	r_2	S	t_{imp}	T	v_2	η	ρ_g
60 cycles / min*	10 min*	410 GPa ^[6.32]	1.38x10 ⁻²³ Nm/K ^[6.18]	101 kPa [#]	6 μm^*	7.6 cm*	1 μs^{**}	291 K [#]	0.1 ^[6.32]	1.8x10 ⁻⁵ Pa.s ^[6.18]	1.2 kg/m ³ ^[6.26]

Table 6.2: Numerical values of the abradant material parameters (**experimentally measured*; ***proposed values for best fit with the experimental data*; [#]*standard conditions*; A.S.: Abrasion speed)

6.5 Model development

For a given material type, surface and abrasion conditions, the equation 1 serves as the fundamental for the present model:

$$N_{air}(d_p) = N(d_p) \cdot P(d_p) \quad \{1\}$$

$N(d_p)$ is the total number of wear particles, with size d_p , generated during abrasion such that $d_p < 1$ mm; $P(d_p)$ is their aerosolization probability; $N_{air}(d_p)$ is the number of aerosol particles with size d_p .

6.5.1. Formulation of $N(d_p)$

6.5.1.1 Total wear volume

The unevenness or roughness of the surface can be represented by the microscopic entities called *asperities*. Their distribution on the surface is generally random. During various studies focused on the surface topography and its wear during abrasion, the asperity distribution has been supposed to follow a normal distribution i.e. assumption *T.1* [6.12-6.14]. This assumption is also supported by the *Central limit theorem* in probability theory which states that under fairly common conditions, the sum of a large number of random variables will have an approximately normal distribution.

Therefore, the asperity height distribution, $f(z)$ can be written as

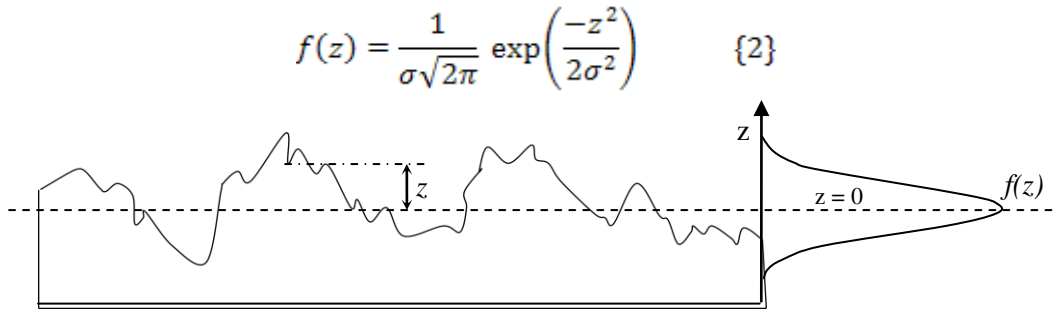


Figure 6.2: Asperity height distribution on a surface of the specimen following a normal distribution

In equation 2, σ represents the standard deviation in the values of the variable z . If ψ is the number density for the asperities, then the number of asperities (dn) having heights in the range z and $z+dz$, linear distance ds and area dA_c ,

$$dn = \psi \cdot f(z) \cdot dz \cdot ds \cdot dA_c$$

According to *Archard wear law*, the wear volume generated from a contact between two solid sliding surfaces is directly proportional to the normal force (F_N) being applied during the abrasion and inversely proportional to the hardness of the material (H) being abraded. Following the assumptions *T.2* and *T.3*, the wear volume generated by dn asperities,

$$dV_w = \frac{KF_N}{H} \psi \cdot f(z) \cdot dz \cdot dA_c \cdot ds \quad \{3\}$$

In equation 3, K is Archard wear constant. It is a dimensionless constant and its numerical value depends upon the type of abrasion conditions which are generally decided by the type of materials getting abraded and the relative sliding velocity. Moreover, its value is always less than 1 [6.35]. The total wear volume can be written as:

$$V_w = \frac{K\psi F_N}{H} \int_0^{A_c} dA_c \int_{z_n}^{z_{max}} f(z) dz \int_0^S ds$$

$$V_w = \frac{K\psi A_c F_N S}{H} \int_{z_n}^{z_{max}} f(z) dz \quad \{4\}$$

In equation 4, z_{max} and z_n represent the height of the highest asperity available on the specimen surface before and after the abrasion respectively.

6.5.1.2 Contact Area

It should be noted that the value of A_c is equal to the sum of all contact areas made by the individual asperities with the abrasant. If a_i is the radius of the contact circle made by the i^{th} asperity with the abrasant, then

$$A_c = \pi \sum a_i^2 \quad \{5\}$$

On the basis of the Tabor parameter, TP [6.36] and following the assumption $T.4$, the value of a can be determined using the JKR criterion (equation 7) [6.37] or DMT criterion (equation 8) [6.38]

$$TP = \left[\frac{\left(\frac{r_1 \cdot r_2}{r_1 + r_2} \right) \gamma^2}{(E^*)^2 Z_0^3} \right]^{1/3} \quad \{6\}$$

$$\gamma = \gamma_1 + \gamma_2 - \gamma_1 \gamma_2$$

$$\frac{1}{E^*} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2}$$

The subscripts 1 and 2 stand for the test sample and abrasant respectively. The variable r (μm) is the radius of the asperities, Z_0 is the constant accounting for a separation distance between two atoms in equilibrium and its value is normally lies in the range $3 - 4 \times 10^{-10}$; γ (J/m^2) is the surface tension; E and ν are the Young's modulus (MPa) and the Poisson's ratio of the test sample respectively. In physical terms, TP represents the magnitude of the elastic deformation compared with the range of surface forces. For the surfaces having large asperity radii with high surface tension, the limiting value of the contact circle radius, a , is decided by the JKR criterion. In such a case, $TP \geq 0.01$. But if the surface is of opposite nature, i.e. small asperity radii with low surface tension, DMT criterion finds its use. Here, $TP < 0.01$. [6.39]

JKR criterion

$$a^3 = \frac{r_1 \cdot r_2}{r_1 + r_2} \cdot \frac{1}{b} \left(F_N + 3\pi\gamma \frac{r_1 \cdot r_2}{r_1 + r_2} + \sqrt{6\pi\gamma F_N \frac{r_1 \cdot r_2}{r_1 + r_2} + \left(3\pi\gamma \frac{r_1 \cdot r_2}{r_1 + r_2} \right)^2} \right) \quad \{7\}$$

$$b = \frac{4}{3\pi(b_1 + b_2)}$$

$$b_1 = \frac{1 - \nu_1^2}{\pi E_1} ; b_2 = \frac{1 - \nu_2^2}{\pi E_2}$$

DMT criterion

$$a^3 = \frac{3}{2} \pi \gamma \left(\frac{r_1 \cdot r_2}{r_1 + r_2} \right)^2 \left(\frac{1 - \nu_1^2}{E} \right) \quad \{8\}$$

Figure 6.3 illustrates changes in asperity height distribution during successive abrasion strokes. With every stroke, height of all those asperities decrease which are in contact with abrasant owing to their wear while the area of their individual contact circles increase. This means that if z_n is the maximum height available at the end of the first stroke of the abrasion and it is z_{n-1} for the second stroke ($z_n > z_{n-1}$), then z_{n-1} replaces z_n in the expression of wear volume for second stroke. Similarly, A_c' (total area of contact before second stroke of the abrasion) replaces A_c (total area of contact before first stroke of the abrasion) and $A_c' > A_c$. If

the assumption *T.6* is considered, one may modify equation 4 and write the total wear volume during the successive abrasion strokes as:

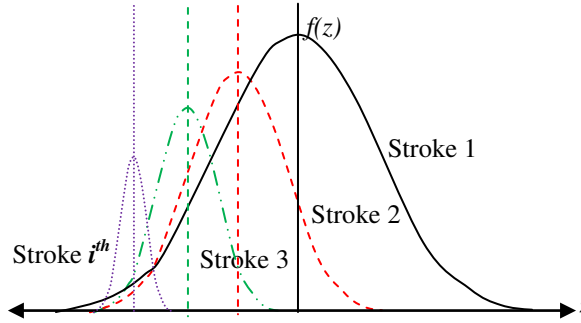


Figure 6.3: Asperities' height redistribution with successive abrasion strokes

$$V_w = \frac{K\psi F_N}{H} \left[S_1 A_c \int_{z_n}^{z_{max}} f(z) dz + S_2 A'_c \int_{z_{n-1}}^{z_n} f(z) dz + S_3 A''_c \int_{z_{n-2}}^{z_{n-1}} f(z) dz + \dots 0 \right] \quad \{9\}$$

$S_1, S_2, S_3 \dots$ denote the abrasion stroke lengths.

6.5.1.3 Aerosolizable and Deposited form of the wear volume

Considering the assumption *T.7* and the experimental results obtained during a series of abrasion experiments done in our laboratory, as also shown in [6.11], it was constantly noted that nearly 99% of the total wear volume was composed of the particles having $d_p > 20 \mu m$ or in other words the *deposited form* of the wear volume i.e. V_{wd} . The remaining 1% had $d_p \leq 20 \mu m$ or in other words the *aerosolizable form* of the wear volume i.e. V_{wa} . Such a behavior continued until a critical value of F_N i.e. $(F_N)_{cr}$ was reached. Beyond this value, if the F_N was increased, the percentage share of the particles having $d_p > 20 \mu m$ started increasing from 99% and consequently for $d_p \leq 20 \mu m$, it started decreasing from 1%. Here, $(F_N)_{cr}$ is the critical value of F_N at which the wear volume generation deviates from the Archard law and becomes non linear [6.11]. On the basis of these experimental observations, following semi-empirical relations can be proposed:

When $F_N \leq (F_N)_{cr}$

$$V_{wa} = 0.01 V_w \quad (for \ d_p \leq 20 \mu m)$$

$$V_{wd} = 0.99 V_w \quad (for \ d_p > 20 \mu m)$$

When $F_N > (F_N)_{cr}$

$$\begin{aligned} V_{wa} &= \left(0.01 - \frac{F_N - (F_N)_{cr}}{7500} \right) V_w \quad (for \ d_p \leq 20 \mu m) \\ &= \left(0.99 + \frac{F_N - (F_N)_{cr}}{7500} \right) V_w \quad (for \ d_p > 20 \mu m) \end{aligned}$$

If $N_a(d_p)$ corresponds to the number of wear particles having total volume V_{wa} and $N_d(d_p)$ corresponds to V_{wd} , then the total number of wear particles with a diameter d_p , can be evaluated by using the assumption *T.5*.

$$N_a(d_p) = \frac{6V_{wa}}{\pi d_p^3} \quad (for\ d_p \leq 20\ \mu m) \quad \{10\}$$

$$N_d(d_p) = \frac{6V_{wd}}{\pi d_p^3} \quad (for\ d_p > 20\ \mu m) \quad \{11\}$$

Rosin-Rammler distribution [6.40], also known as *modified Weibull distribution*, is widely used to describe the size distributions of the micro-sized particles generated in comminution process like grinding, crushing etc. [6.18, 6.41]. According to Rosin-Rammler distribution,

$$p(d_p, P_{80}, m) = 1 - \exp \left\{ \ln(0.2) \left(\frac{d_p}{P_{80}} \right)^m \right\} \quad \{12\}$$

In equation 12, P_{80} ($= 16.784\ \mu m$) is the 80th percentile of the generated wear particles diameter range and m is a parameter which is conventionally used to describe the spread of the Rosin-Rammler distribution [6.40]. If the value of m is high, the size distribution is narrow and it shifts towards the bigger sizes. This is exactly the same behavior one observes while increasing *abrasion severity* [6.11]. Hence, m can also be used as the “*abrasion severity*” describing parameter i.e. higher the value of m , higher is the abrasion severity. Under low normal force or mild abrasion conditions, we propose that

$$m = 1, 2 \quad for\ F_N \leq (F_N)_{cr} \quad \{13\}$$

And under high normal load or severe abrasion conditions, its value is proposed to be,

$$m = 2 + \frac{F_N - (F_N)_{cr}}{\max\{F_N\} - (F_N)_{cr}}, \quad for\ F_N > (F_N)_{cr} \quad \{14\}$$

The values and the empirical relations, proposed for m in the equations 13 and 14, are obtained on the basis of the experimental data fit approximations. It should also be noted that very high relative sliding velocities during abrasion can also have a direct impact on the value of m . But if the abrasion speeds are kept low, m is almost independent of it, as considered in the present case. The function $\max\{F_N\}$ returns the maximum permissible value of F_N which can be applied on a material without its macroscopic failure. If the assumption *P.1* is considered here to describe the size distribution of the wear particles,

$$\begin{aligned} N(d_p) &= N_a(d_p) \cdot p(d_p, P_{80}, m) & d_p \leq 20\ \mu m \\ &= N_d(d_p) \cdot p(d_p, P_{80}, m) & d_p > 20\ \mu m \end{aligned} \quad \{15\}$$

In figures 6.4 (a) and (b), equation 15 is plotted as a function of the particle size for three different materials- brick, wood and stainless steel. Although the particle size range can be varied in much larger size range, here it is shown to vary from 4 nm to 60 μm . The normal force value is always 12 N for these three test samples. The $(F_N)_{cr}$ values for the brick, stainless steel and wood samples, as mentioned in the table 6.1, are 12 N, 25 N and 8 N respectively. The calculated values of the abrasion severity describing parameter i.e. m for these samples in the same order are 2, 2 and 2.75 respectively. If these values of m are considered along with figure 6.4 (a), one may say that increase in the value of m leads to a change in the shape of the size distribution curve. In other words, when the curves corresponding to the brick and stainless steel sample are compared, where m holds the same

value ($= 2$), we observe two approximately parallel size distribution curves i.e. translation from higher values of $N(d_p)$ to the lower ones. However, in the case of the wood sample where the value of m increases from 2 to 2.75, the corresponding size distribution curve is no longer parallel to the two precedent ones but rotated in a counterclockwise direction around a pivot point of $3 \mu\text{m}$. This observation shall be discussed in more details in the sections 6.6.3.1, 6.6.3.2 and 6.6.3.3 where, through the parametric studies on m , a gradual change in the size distribution curves are shown with the changes in the value of m .

From figure 6.4 (a), the number of wear particles generated during the abrasion of the brick, is always greater than that of wood and stainless steel over the entire size range. In the case of latter two, the number of particles having $d_p < 3 \mu\text{m}$ is greater for stainless steel but the number of particles having $d_p > 3 \mu\text{m}$ is greater for the wood.

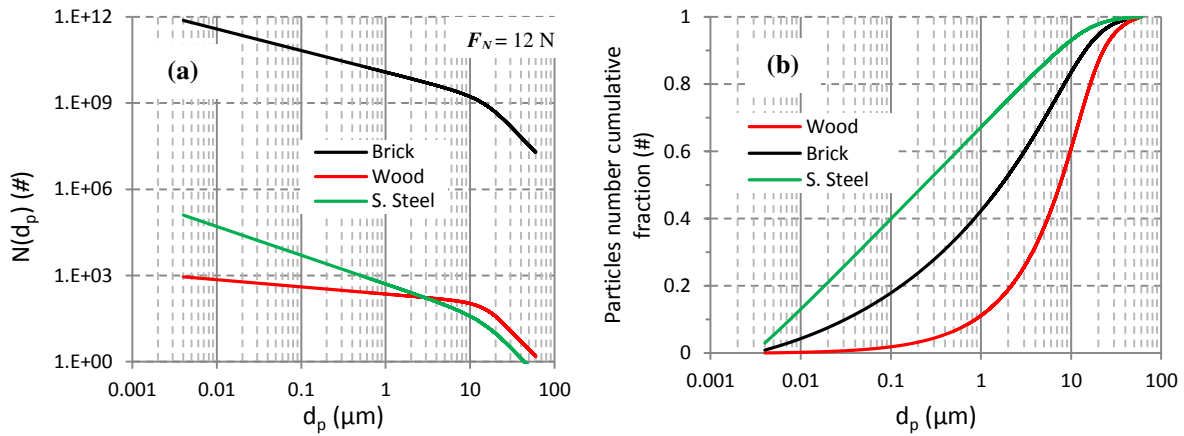


Figure 6.4 (a): Size distribution of $N(d_p)$ and (b) $N(d_p)$ cumulative fraction for brick, wood and stain steel test samples as predicted by equation 15

If this observation is considered with $3 \mu\text{m}$ as the deciding size limit for the smaller and bigger sized particles, one may conclude that for the three materials, the brick generates the highest number of both smaller as well as bigger sized wear particles, followed by the stainless steel which generates higher number of smaller sized wear particles and then the wood which generates higher number of bigger sized wear particles.

In figure 6.4 (b), cumulative fraction of the number of wear particles is shown as a function of the particle size. Table 6.3 shows the informations that one may retrieve from the figure 6.4 (b). While for the material order as stainless steel to brick to wood, 90% of the number of wear particles has a size that increases in this order, the percentage of the number of wear particles having size $< 100 \text{ nm}$ is decreasing for the same material order. Therefore, one may clearly observe the effect of the material type as the abrasion conditions, for these three materials, are exactly same. A study to test the sensibility of different parameters that define the material type has also been carried out which shall be discussed later in the section 6.6.4 for the three materials.

Material	90% of the number of wear particles have a size less than or equal to	% of the number of wear particles having size $< 100 \text{ nm}$
Stainless Steel	$7.3 \mu\text{m}$	40%
Brick	$14.3 \mu\text{m}$	18%
Wood	$23 \mu\text{m}$	2%

Table 6.3: Effect of the material type on the predicted size dist. of the wear particles as seen in figure 6.4 (b)

It should be noted that we haven't experimentally measured the size distribution of the wear particles since the present study is focused on the aerosol particles. Therefore, no comparison of the theoretically calculated data, shown in figures 6.4 (a) and (b), is done with the experimentally measured ones. However, for comparison, the results shown in table 6.3, can be compared with other experimental results available in literature. It has been observed that most of the times, the size distributions which have been determined experimentally, were done on the basis of microscopy in which the sampled wear particles were deposited on a suitable surface and by using some statistical analyses or image correlation methods, the size distributions were determined.

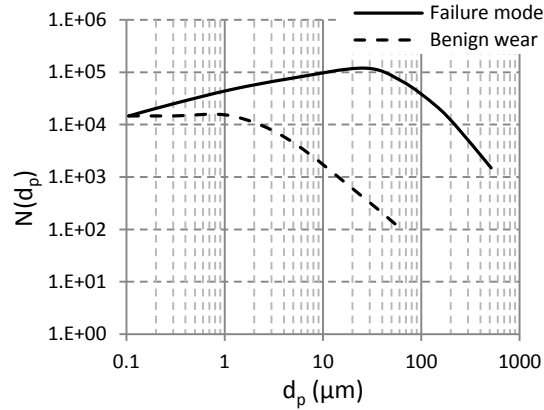


Figure 6.5: Change in wear particles size distribution as running hours accumulate during the abrasion of an iron based alloy test sample [6.42]

For example, [6.41] determined size distributions for polyethylene wear particles from hip simulator models. They found 90% of the number of the wear particles had a size less than or equal to 2.2 μm . Another study [6.42], done using spectrographic analysis of the oil samples containing wear particles generated from the abrasion of stainless steel samples showed the size distributions to be varying with severity of the abrasion, as shown in figure 6.5. The material tested here is an iron based alloy. In addition to the factors accounted in the section 6.5.1.3, here the reason for the increase in the abrasion severity is the increase in abrasion duration which induces a *ratcheting* effect i.e. the accumulation of the net plastic strain in the surface asperities with successive abrasion strokes. This phenomenon is beyond the scope of this thesis. When the abrasion conditions changes from benign or mild to failure mode or severe, the size distribution curve not only translates but also rotates counterclockwise- a similar behavior observed in the case of figure 6.4 (a).

6.5.2. Formulation of $P(d_p)$

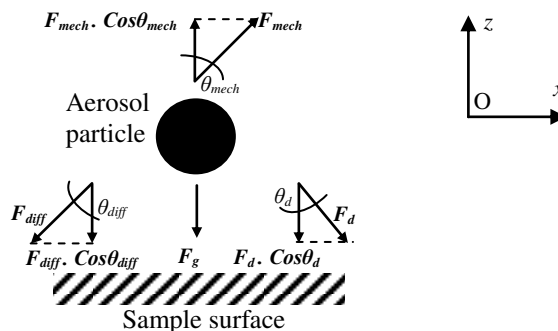


Figure 6.6: Action of different forces acting on a particle while getting aerosolized

While getting aerosolized, all the particles do not have same aerosolization probability due to various size dependent physical phenomena like diffusion, sedimentation, drag, agglomeration etc. It is believed here that the actual aerosolization probability of these particles is a function of the resultant of four forces- Gravitational force (F_g), Drag Force (F_d), Diffusive force (F_{diff}) and Mechanical force input (F_{mech}). These force act on the wear particles simultaneously as soon as they are generated during abrasion. Figure 6.6 illustrates the case.

6.5.2.1 Gravitational force

The gravitational force, F_g , is proportional to particle mass, m_p , and gravitational acceleration, g ,

$$F_g = m_p g = \frac{\pi}{6} d_p^3 (\rho_p - \rho_g) g \quad \{16\}$$

This force exerts a *pulling action* on the wear particle towards the surface and thus opposes its tendency to get released in air.

6.5.2.2 Drag force

The drag force, F_d , or air resistance, refers to the force that opposes the relative motion of a particle in air or gas. This force is induced by the motion of the particle, and acts in the opposite direction of motion. It is a function of a particle's velocity with respect to the gas surrounding it. According to a modified *Stokes' law* [6.18],

$$F_d = \frac{\pi}{8} C_d \rho_g V^2 d_p^2 \quad \{17\}$$

C_d is known as *drag coefficient* and

$$C_d = \frac{24}{Re_p}$$

V is the particle *settling velocity* and

$$V = \frac{\rho_p d_p^2 g C_c}{18\eta}$$

Re_p is the particle *Reynolds number* and

$$Re_p = 65000 \times V \times d_p$$

C_c is the slip correction factor which considers the particle *slip* through the space between the molecules before colliding with another molecule or object in its path. This effectively leads to increased velocity of the particle and reduced drag force compared to that predicted by the *Stokes' law*.

$$C_c = 1 + \frac{1}{p d_p} [15.6 + 7e^{(-0.059 p d_p)}] \quad \{18\}$$

p is the atmospheric pressure; η is the air viscosity coefficient and its value is 1.82×10^{-5} Pa.s.

6.5.2.3 Diffusive force

Nanoparticles can achieve significant diffusive motion in much the same manner as that described for gas molecules. Because of their large inertia and surface area over which bombardment by the gas molecules is averaged, large particles diffuse more slowly than small ones in the air. The particles' diffusivity, D , can be computed by

$$D = kTB \quad \{19\}$$

k is the Boltzmann constant and its value is 1.38×10^{-23} N.m/K; T is the temperature in Kelvin and B is the mechanical mobility of a particle. The mechanical mobility of a particle can be defined as the velocity produced by a unit force on the particle, and mathematically, it can be written as

$$B = \frac{C_c}{3\pi\eta d_p} \quad \{20\}$$

The *root mean square (rms) distance*, x_{rms} , travelled by the particles in time t_{imp} ,

$$x_{rms} = \sqrt{2Dt_{imp}}$$

The value of a diffusive force can be calculated as

$$F_{diff} = m_p \frac{\partial^2}{\partial t^2} \sqrt{2Dt_{imp}} = -m_p \frac{\sqrt{D}}{2\sqrt{2}} t_{imp}^{-3/2} \quad \{21\}$$

In equation 21, F_{diff} is negative which means that it resists particle aerosolization in the present case. Its magnitude is equal to its modulus i.e.

$$|F_{diff}| = m_p \frac{\sqrt{D}}{2\sqrt{2}} t_{imp}^{-3/2} \quad \{22\}$$

6.5.2.4 Mechanical force input

The influence of the abrasant with the wear particles plays an important role during their aerosolization. When the abrasant starts sliding over a sample surface, it impacts the surface asperities with a certain force. As a result, the asperities undergo certain irreversible deformation, termed as *plastic deformation*.

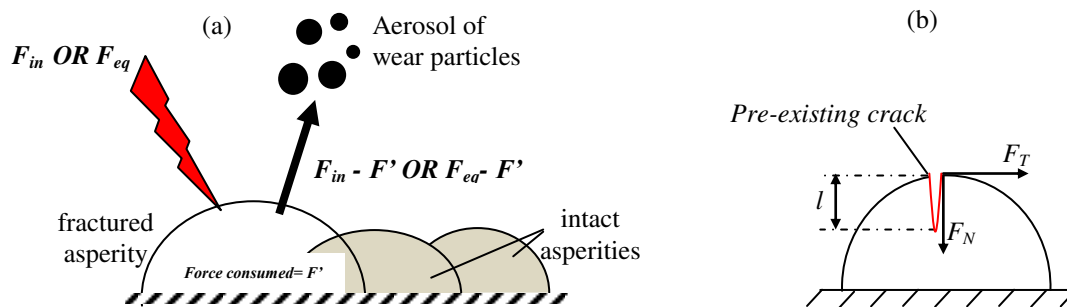


Figure 6.7 (a): Fracturing of the asperity and consumption of a part of the mechanical force provided via abrasion (b): Force state acting on the pre-existing crack in the asperity

A conceptual model has been presented in [6.11] which explains how such a deformation leads to the fracturing of the asperity in small fractions. This conceptual model lays the foundation the assumption *P.2*. This fracture can be *brittle* (i.e. no apparent plastic deformation taking place before fracture) or *ductile* (i.e. extensive plastic deformation taking place before fracture), depending upon the nature of the asperity to undergo plastic deformation. As mentioned by the assumption *P.3*, a part of the force applied through the abrasant is consumed in this fracturing (i.e. F') while the remaining part acts on the particles generated after fracturing. This is illustrated in figure 6.7 (a).

In the case of a *brittle or elastic material*, the force applied through the abrasant can be expressed in terms of F_{in} where

$$F_{in} = \sqrt{F_N^2 + F_T^2} \quad \{23\}$$

F_T is the tangential force acting during abrasion. The force consumed during brittle fracture can be calculated using [6.20] in which the energy absorbed during the fragmentation of the brittle spheres (E_a) is calculated as

$$E_a = \frac{4}{5} \left\{ \frac{3}{4} \right\}^{2/3} F_{in}^{5/3} \left(\frac{r_1 \cdot r_2}{r_1 + r_2} \right)^{1/3} (E^*)^{2/3} \quad \{24\}$$

If x_c is the critical crack length passing through an asperity beyond which the asperity fails and gets fragmented,

$$x_c = \pi \left(\frac{\sigma_s Y}{K_C} \right)^2$$

Here, σ_s is the stress being applied; Y is a constant and for pre-existing cracks present in the form of notches, its value can be considered as 1.12 (as mentioned in the assumption *P.4*); K_C is the fracture toughness of an asperity and it can be defined as the resistance of a material to failure from fracture.

Therefore, the force required to produce a crack length, x_c , in a brittle asperity,

$$F' = \frac{E_a}{x_c} = \frac{4}{5} \left\{ \frac{3}{4} \right\}^{2/3} F_{in}^{5/3} (E^*)^{2/3} (r^*)^{1/3} \frac{1}{\pi} \left(\frac{K_C}{Y \sigma_s} \right)^2 \quad \{25\}$$

However, in the case of a *ductile or elastoplastic material*, prior to the fracturing, the asperities are susceptible to their plastic deformation or *yielding*. The amount of the energy absorbed is much greater than in the case of brittle fracture. One of most used criteria to predict this yielding is the *von Mises yield criterion*. It says that a material starts yielding when the stress corresponding to F_{eq} (equation 26) becomes equal or greater than the *yield strength*, σ_y , of the material. The yield strength is the stress at which a material begins to deform plastically.

$$F_{eq} = \sqrt{F_N^2 + 3F_T^2} \quad \{26\}$$

In the present case, we assume that a pre-existing and vertically aligned crack is present in the asperity that has a length l . Moreover, during abrasion, both F_N and F_T are acting simultaneously on it. The condition is shown in figure 6.7 (b). If the crack were to propagate from this pre-existing crack only, leading the asperity to fail, it would be under the mixed

effect of both forces. This is a classical case of fracture mechanics which terms this condition as *mixed mode fracture*. The two modes are Mode I and Mode II which are contributed by F_T and F_N respectively. The stress intensities, contributed by each mode, are measured in terms of stress intensity factors, K_I and K_2 . More details on the fracture modes can be found in [6.43].

The only parameter on which the propagation of this pre-existing crack in an asperity depends is the fracture toughness of the asperity. For a crack to propagate, the stress intensity around the crack tip must exceed K_c . One may calculate the magnitude of K_c from the *G-criterion* that relates K_c to the stress intensity factors for the two modes. This failure criterion is written as

$$K_c^2 = K_1^2 + K_2^2$$

$$K_1 = \frac{2F_T}{\sqrt{2\pi l^3}}; K_2 = \frac{2F_N}{\sqrt{2\pi l^3}}$$

To evaluate F' for a ductile asperity, the *Griffith's criterion* can be applied which suggests that

$$F' = \left[\underbrace{\sigma_y}_{\text{Plastic Deformation}} + \underbrace{\sqrt{\frac{2K_c^2 \sigma_y^2}{\pi l (\sigma^2 + 2\sigma_y^2)}}}_{\text{Ductile Fracturing}} \right] A_c \quad \{27\}$$

Also from equation 20, B , the mechanical mobility of a particle, was defined as the velocity produced by a unit force on an aerosol particle. Therefore, for a force having magnitude equal to $F_{in} - F'$ (in the case of brittle fracture) or $F_{eq} - F'$ (in the case of ductile fracture) and acting during the period in which the abrasant and the asperity are in contact (t_{imp}), the total mechanical force transmitted to a wear particle,

$$F_{mech} = \frac{B m_p (F_{in} - F')}{t_{imp}} \text{ or } \frac{B m_p (F_{eq} - F')}{t_{imp}} \quad \{28\}$$

It should be noted that here we have introduced a *hypothetical* parameter t_{imp} , as also introduced before in the context of the diffusive force. The main objective of introducing it is that it may serve as a parameter that accounts for the *abrasion speed*. Higher the abrasion speed, lower is the value of t_{imp} . If one may set a reference value of t_{imp} for a particular value of the abrasion speed, different values of t_{imp} , corresponding to other values of the abrasion speed, can also be deduced. For example, if $1 \mu s$ is the reference value of t_{imp} that corresponds to 0.2 m/s of the abrasion speed, then $t_{imp} = 0.5 \mu s$ would correspond to 0.4 m/s of the abrasion speed or $t_{imp} = 2 \mu s$ would correspond to 0.1 m/s .

6.5.2.5 Aerosolization criterion

Now, for a wear particle to get released or aerosolize from the sample surface,

$$F_{mech} \cdot \cos \theta_{mech} \geq F_g + F_d \cdot \cos \theta_d + F_{diff} \cdot \cos \theta_{diff} \quad \{29\}$$

From the equations 13, 14, 22, 28, 29 and taking $\theta_i = 0$ (to avoid the complications),

$$m_p \leq \frac{2[pd_p + 15.6 + 7e^{-0.059pd_p}] \left[9(F_{in} - F') - \pi k T t_{imp}^{-1/2} \right]}{9t_{imp} \pi g d_p^4 [\eta \pi p d_p (\rho_p - \rho_g) + 48 \times 10^{-6} \rho_p \rho_g (pd_p + 15.6 + 7e^{-0.059pd_p})]} = (m_p)_{max}$$

For n asperities fractured during abrasion,

$$(m_p)_{max} = \frac{2n[pd_p + 15.6 + 7e^{-0.059pd_p}] \left[9(F_{in} - F') - \pi k T t_{imp}^{-1/2} \right]}{9t_{imp} \pi g d_p^4 [\eta \pi p d_p (\rho_p - \rho_g) + 48 \times 10^{-6} \rho_p \rho_g (pd_p + 15.6 + 7e^{-0.059pd_p})]} \quad \{30a\}$$

(brittle fracture)

or

$$= \frac{2n[pd_p + 15.6 + 7e^{-0.059pd_p}] \left[9(F_{eq} - F') - \pi k T t_{imp}^{-1/2} \right]}{9t_{imp} \pi g d_p^4 [\eta \pi p d_p (\rho_p - \rho_g) + 48 \times 10^{-6} \rho_p \rho_g (pd_p + 15.6 + 7e^{-0.059pd_p})]} \quad \{30b\}$$

(ductile fracture)

$$n = \psi A_c \int_{z_n}^{z_{max}} f(z) dz \int_0^S ds$$

The corresponding number of aerosol particles,

$$N'(d_p) = \frac{6 (m_p)_{max}}{\pi d_p^3 \rho_p} \quad \{31\}$$

For equation 31 to represent number size distribution of the aerosol particles, it is modified using a gamma distribution function (assumption A.1), shown in equation 32.

$$g(d_p, \epsilon, \emptyset) = \frac{1}{\emptyset^\epsilon} \frac{1}{\Gamma(\epsilon)} d_p^{\epsilon-1} \exp\left(\frac{-d_p^{0.2}}{\emptyset}\right) \quad \{32\}$$

ϵ and $\emptyset$ are shape and scale parameters of the distribution curve; $\Gamma(\epsilon)$ is the gamma function evaluated at ϵ .

Like m , the values of ϵ and $\emptyset$ are also proposed here on the basis of the experimental data fit, therefore,

$$\epsilon = 10.5; \emptyset = 0.07 \quad F_N \leq (F_N)_{cr}$$

$$\epsilon = 10.5 + \frac{F_N - (F_N)_{cr}}{10} \quad F_N > (F_N)_{cr}$$

$$\emptyset = 0.07 + \frac{F_N - (F_N)_{cr}}{1000}$$

Hence, the aerosolization probability can be written as,

$$P(d_p) = \frac{N'(d_p) \cdot g(d_p, \epsilon, \emptyset)}{\max[N'(d_p) \cdot g(d_p, \epsilon, \emptyset)]} \quad \{33\}$$

In figure 6.8 (a), equation 33 is plotted as a function of the particle size for the same three materials with $F_N = 12$ N. For the comparison, $t = 1$ for the wood sample. The same graph is replotted in figure 6.8 (b), except the log scale has been removed on y-axis. Although the particle size range can be varied in much larger size range, here it is shown to vary from 4 nm to 30 μm . From figures 6.8 (a) and (b), a clear effect of the particle size and thus the four forces can be observed as the aerosolization is almost 100 % in an intermediate particle size range which is 1 to 2 μm (for brick), 1 to 1.5 μm for wood and 0.4 to 0.6 μm for stainless steel. Infact, $P(d_p)$ is 100% for $d_p = 1.538$ μm (for brick), 1.283 μm (for wood) and 0.512 μm (for stainless steel). If d_p is smaller or bigger than the above mentioned size ranges, the $P(d_p)$ decreases. For a smaller sized particle, it is the diffusive force that dominates to resist the aerosolization whereas for a bigger sized particle, it is the gravitation force that dominates. Among these three materials, when $d_p < 1\mu\text{m}$, $P(d_p)$ always holds a maximum value for the stainless steel, which is followed by wood and then brick. But when $d_p > 1\mu\text{m}$, the order is brick, wood and then stainless steel.

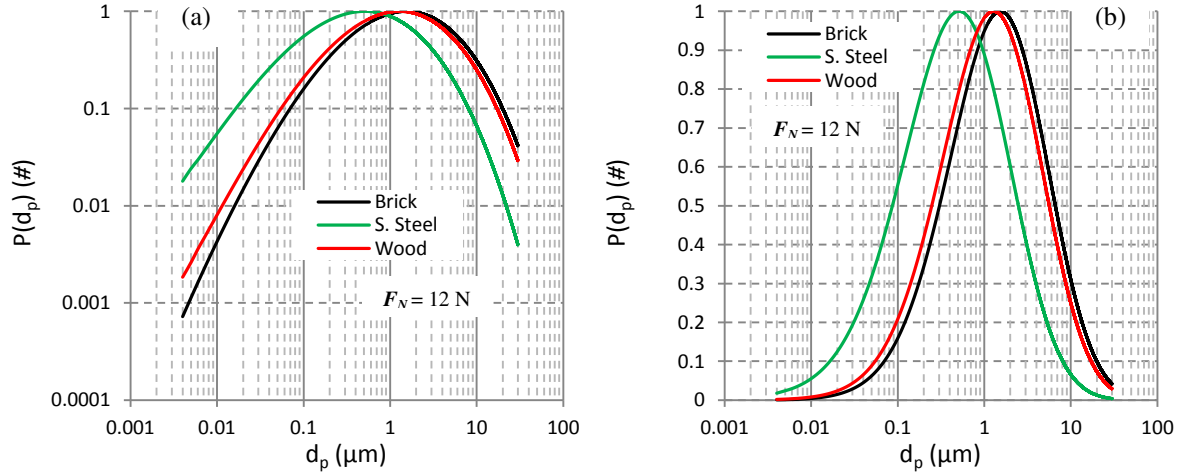


Figure 6.8 (a): Size distribution of $P(d_p)$ with both axes on logarithmic scale **(b)** x-axis on logarithmic scale as predicted by equation 33

6.5.3. Formulation of $N_{air}(d_p)$

From the equations 1, 15, 33 and assumptions A.2 and A.3,

$$N_{air}(d_p) = N_a(d_p) \cdot p(d_p, P_{80}, m) \cdot \frac{N'(d_p) \cdot g(d_p, \epsilon, \emptyset)}{\max[N'(d_p) \cdot g(d_p, \epsilon, \emptyset)]} \quad \{34\}$$

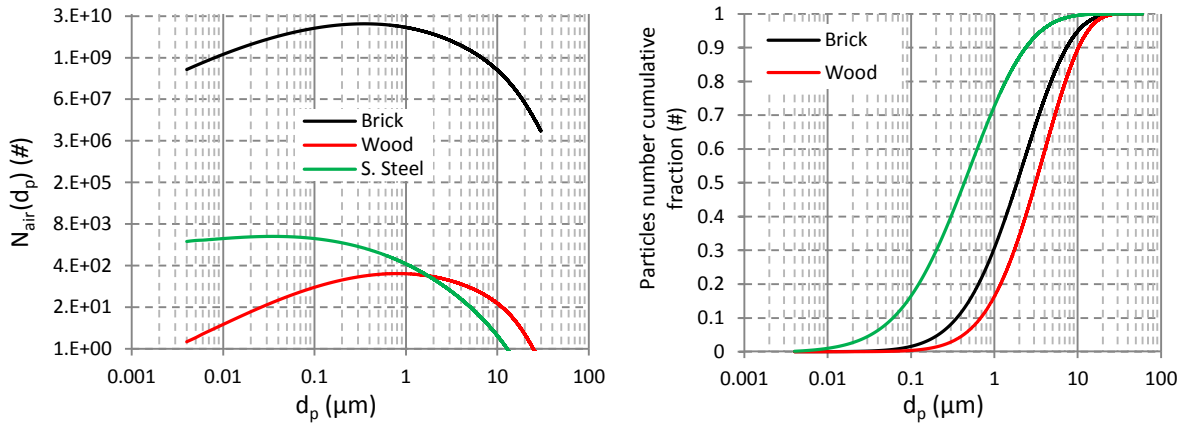


Figure 6.9 (a): Size distribution of $N_{air}(d_p)$ and **(b)** cumulative fraction of $N_{air}(d_p)$ for brick, wood and stain steel test samples as predicted by equation 34

In figure 6.9 (a), equation 34 is plotted as a function of the particle size for the same three materials with $F_N = 12$ N. It appears to follow the same pattern as seen in the figure 6.4 (a), except for the deciding size limit for the smaller and bigger sized particles in case of wood and stainless steel. The size limit, which was $3 \mu\text{m}$ in the case of figure 6.4 (a), is now $1.3 \mu\text{m}$. In figure 6.9 (b), the size distribution of the cumulative fraction of $N_{air}(d_p)$, for the three materials, is shown. As one may see, in table 6.4, 90% of the number of aerosol particles has a size which is lower than the corresponding size in the case of wear particles for the three materials (table 6.3). Not only this, the cumulative percentage of the particles having size < 100 nm is also lower.

Therefore, it can be concluded that by applying the present aerosolization criterion (equation 29), to obtain the number of aerosol particles, not only scales down the size distribution of the wear particles (i.e. reduction in $N(d_p)$) but also shifts it towards the smaller particle sizes.

Material	90% of the number of aerosol particles have a size less than or equal to	% of the number of aerosol particles having size < 100 nm
Stainless Steel	$2.4 \mu\text{m}$	16%
Brick	$7.4 \mu\text{m}$	1.5%
Wood	$10.2 \mu\text{m}$	0.4%

Table 6.4: Effect of the material type on the size distribution of the aerosol particles as seen in figure 6.9 (b)

6.6 Model output

6.6.1 Choice of materials to test

The choice of the materials has been done on the basis of their *plasticity index*. The plasticity index of a material, under a stress, is the measure of its tendency towards consequent plastic deformation. Higher is its value, higher is the possibility of the plastic flow at the asperity contacts. Plasticity index,

$$\omega = \frac{E^*}{H} \left(\frac{\sigma}{r} \right)^{1/2} \quad \{35\}$$

$$E^* = \frac{E_1 \cdot E_2}{E_2(1 - \nu_1^2) + E_1(1 - \nu_2^2)}$$

According to [6.44], the materials for which $0 < \omega < 0.6$, there is never a plastic deformation at the asperities' contacts with the abradant. Infact, as soon as the stress at the contacts reaches the yield limit, the fracture propagates and the asperity fails to withstand further load. For $0.6 < \omega < 1$, the plastic deformation may occur under mild abrasion conditions i.e. when $F_N \leq (F_N)_{cr}$. For $\omega > 1$, the abrasion is always accompanied by the plastic deformation at the asperities' contacts with the abradant, irrespective of the value of F_N . In table 6.5, ω is calculated for the three materials using equation 35.

Materials	E_1 (GPa)	E_2 (GPa)	ν_1 (#)	ν_2 (#)	H (HV)	σ (μm)	r_1 (μm)	ω
Brick	1.5 ^[6.21]	410 ^[6.32]	0.2 ^[6.21]	0.1 ^[6.32]	800 ^[6.21]	14	7	0.27
Wood	1 ^[6.22]	410 ^[6.32]	0.7 ^[6.22]	0.1 ^[6.32]	520 ^[6.24]	32	11	0.64
S. Steel	200 ^[6.23]	410 ^[6.32]	0.6 ^[6.23]	0.1 ^[6.32]	1200 ^[6.23]	0.008	0.03	7.663

Table 6.5: Values of the parameters for calculating plasticity index

Thus by choosing these three materials to test the model output, we cover a broad range of material types that spans from completely elastic to completely plastic behavior during abrasion.

6.6.2 Comparison with Experimental Results

6.6.2.1 Brick

In figure 6.10, a comparison between experimentally measured (using aforescribed experimental set-up) and theoretically calculated (using equation 34) size distribution of the emitted aerosol particles is done. A close agreement between the two is clearly visible.

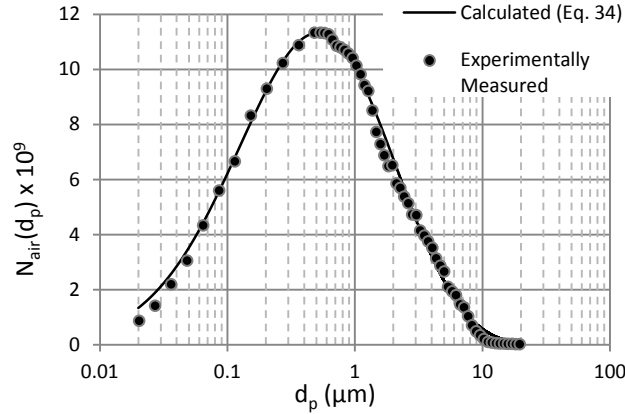


Figure 6.10: Comparison between experimentally measured and theoretically calculated (eq. 34) size distributions of the aerosol particles generated during the abrasion of brick

6.6.2.2 Wood

With respect to the brick, the abrasion and hence the particle emission behavior of the wood sample is completely different. The two particle sizers used for the experimental particles emission characterization- SMPS and APS- have sampling times of 120 s and 5 s respectively for one scan. For these instruments to operate, the total number of aerosol particles (i.e. total $N_{air}(d_p)$) should get generated at an almost constant rate, at least for a duration equal to their sampling times. For the brick sample, the total $N_{air}(d_p)$ was always constant as long as the abrasion continued. However, for the wood sample, that's not the case, as shown in figure

6.11 (a). Therefore, experimental evaluation of the size distribution of emitted aerosol particles from the wood sample is not possible. But if the size distribution were to be determined, a theoretical evaluation can be done by using the present model. Moreover, one may also retrieve the information on the evolution of the size distribution with time. This is shown in figure 6.11 (b) for a particle size range of 4 nm to 3 μm . The experimental data, present in figure 6.11 (a), is compared to the theoretical one (obtained using equation 34) in figure 6.11 (c). A close agreement between the two types of data can again be seen.

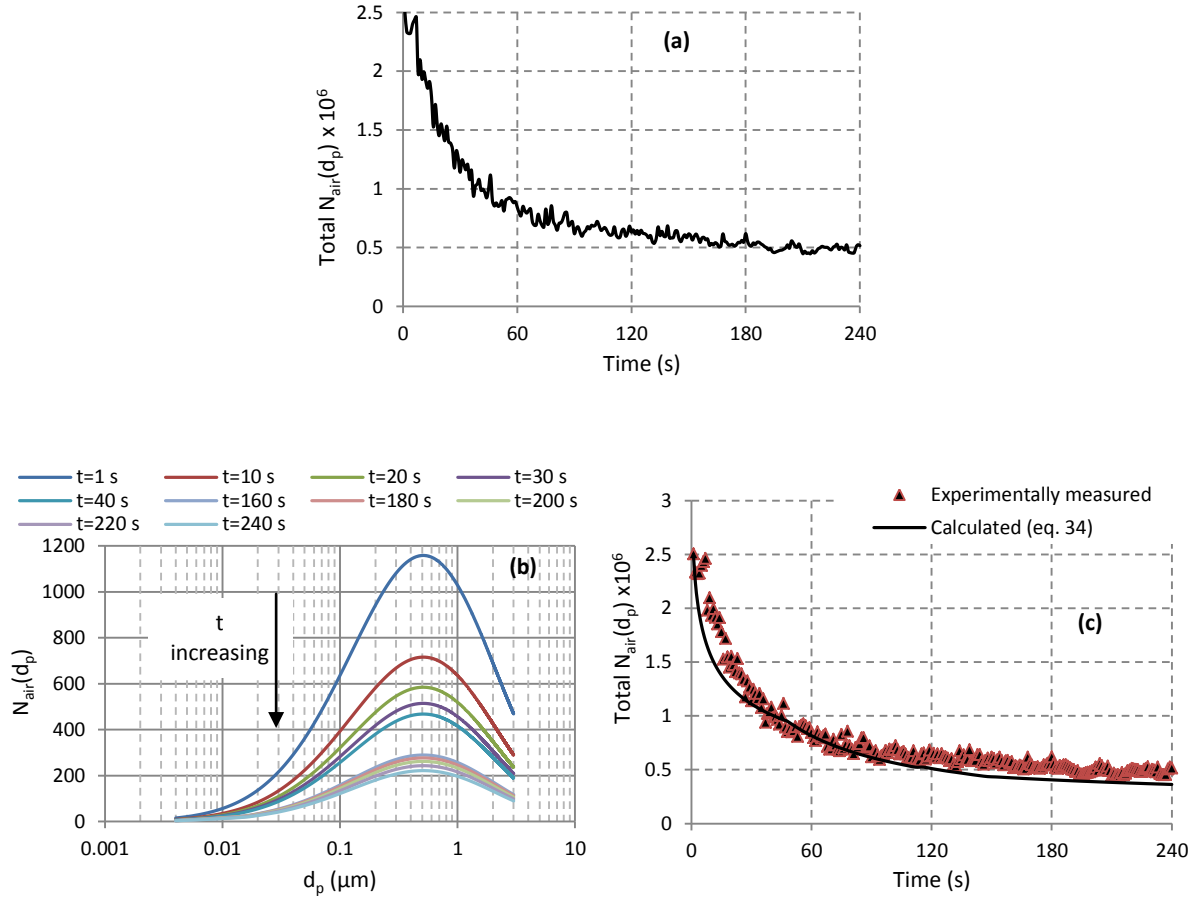


Figure 6.11 (a): Experimentally measured variation of the total number of the aerosol particles (4 nm to 3 μm) with time (b): Simulated or theoretically calculated evolution of the emitted aerosol particle size distribution with time (c): Comparison between experimentally measured and theoretically calculated (eq. 34) total number of the aerosol particles generated from the abrasion of wood

6.6.2.3 Stainless steel

Like wood, determination of the size distribution of the aerosol particles, for a stainless steel specimen, is also not possible due to a low number of the emitted aerosol particles during abrasion tests. Such a low number makes it difficult for the particles sizers to detect a particle. Therefore, here also, a comparison between experimentally measured and theoretically calculated total number of aerosol particles is shown in figure 6.12. A time constant total number of aerosol particles can be seen with a close agreement between the two types of data.

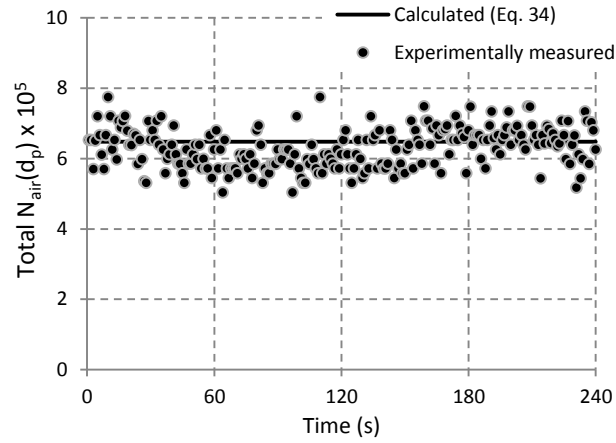
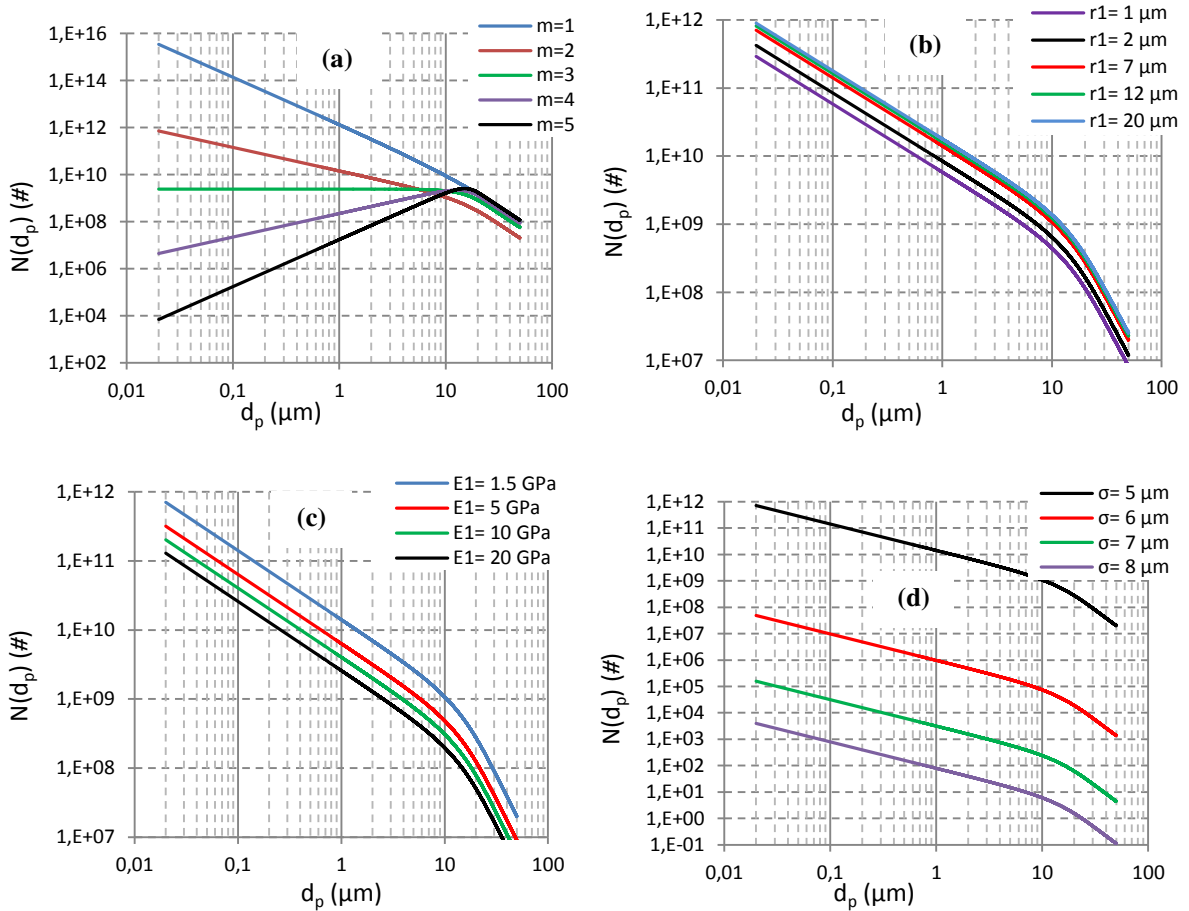


Figure 6.12: Comparison between experimentally measured and theoretically calculated (eq. 34) size distribution of the aerosol particles generated from the abrasion of stainless steel

6.6.3 Simulation

6.6.3.1 Brick

6.6.3.1.1 Wear debris particles, $N(d_p)$



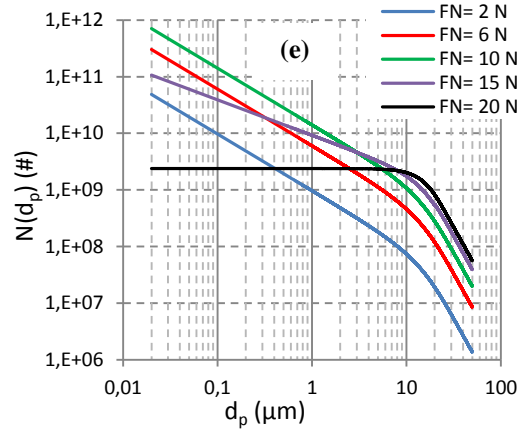


Figure 6.13: Effect of (a) m (b) rms radius of the surface asperities (c) sample surface Young's Modulus (d) std. dev. in the sample surface asperity heights distribution (e) normal force on the number-size distribution of the wear particles generated during the abrasion of brick (determined using equation 15)

In figure 6.13 (a), the effect of the variation of m - the proposed variable accounting for the severity of the abrasion- on the distribution of $N(d_p)$, over a particle size range of 20 nm to 35 μm , is simulated. Ranging on a scale from 1 to 5, lower values of m ($m=1, 2, 3$) correspond to the light abrasion conditions whereas higher ones correspond to the severe abrasion conditions ($m=4, 5$). As the value of m changes from 1 to 2, $N(d_p)$ for both size ranges, $d_p < 20 \mu\text{m}$ and $d_p > 20 \mu\text{m}$, decreases. With $m=3$, $N(d_p)$ for the size range $d_p < 20 \mu\text{m}$ continue to decrease but it starts increasing for the size range $d_p > 20 \mu\text{m}$. With a further increase in m ($m=4, 5$), $N(d_p)$ for the size range $d_p < 20 \mu\text{m}$ keeps on decreasing but it remains almost constant for the size range $d_p > 20 \mu\text{m}$. From these observations, one may conclude that increasing the severity of the abrasion conditions leads to the generation of bigger sized particles ($d_p > 20 \mu\text{m}$).

In figure 6.13 (b), the effect of increasing surface asperity root mean square (rms) radius (r_I), on the distribution of $N(d_p)$, is simulated. The increasing values of $N(d_p)$ can be observed with increasing r_I . It should also be noted from the figure 6.13 (b) that as the value of r_I approaches higher values ($r_I \geq 7 \mu\text{m}$), the effect of the increasing r_I , on $N(d_p)$, starts to get saturated.

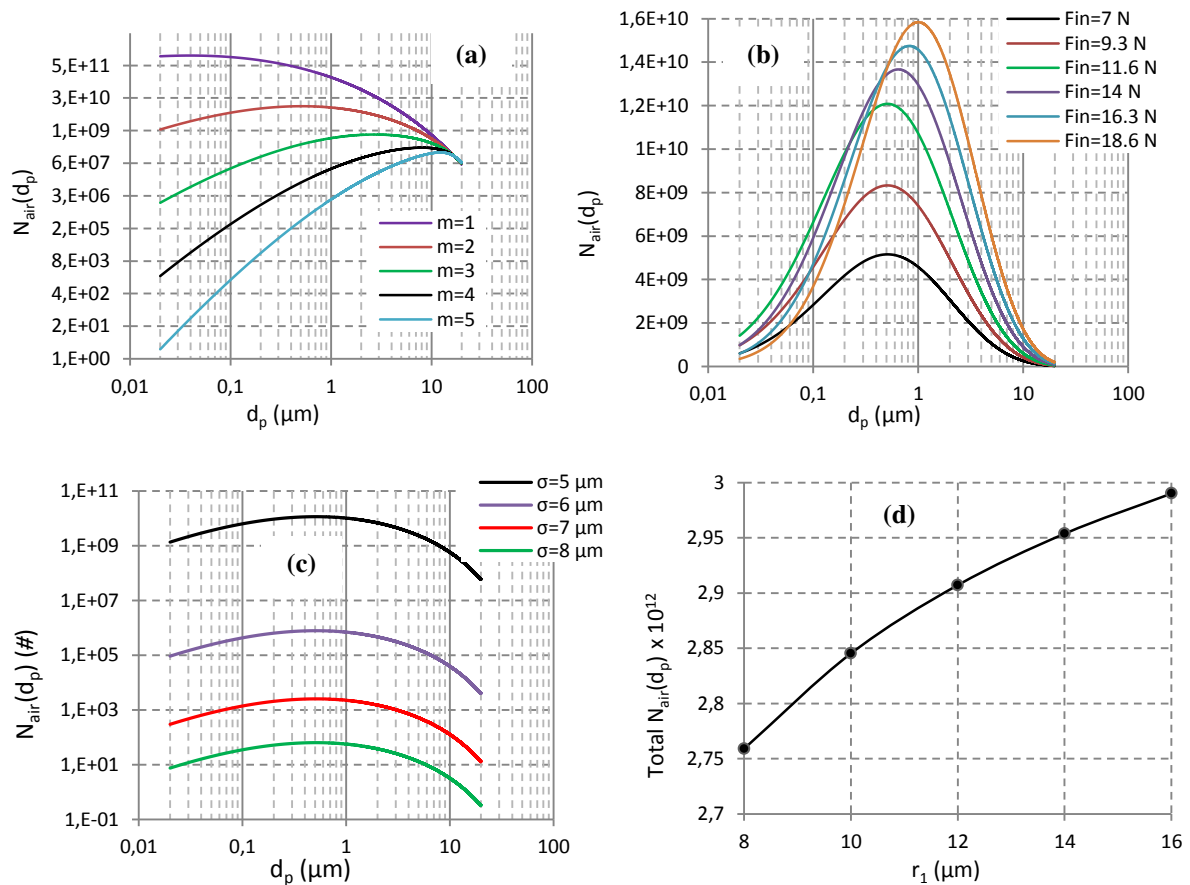
Simulations on the effect of the sample surface elastic modulus (E_I) and the standard deviation in the sample surface asperity heights' distribution (σ) are shown in the figure 6.13 (c) and (d) respectively. Clearly, both of these parameters have a negative correlation with $N(d_p)$.

Since the value of m is considered to depend upon the value of F_N , therefore, as expected, the effect of F_N on the size distribution of $N(d_p)$, is somewhat similar to that of m . This is shown in figure 6.13 (e). For lower values of F_N ($F_N=2, 6$ and 10 N) or $F_N < (F_N)_{cr}$, increasing F_N leads to the increase in $N(d_p)$. For higher values of F_N ($F_N=15$ and 20 N) or $F_N > (F_N)_{cr}$, $N(d_p)$ for the size range $d_p > 3 \mu\text{m}$ continue to increase but it decreases for the size range $d_p < 3 \mu\text{m}$. In the case of $F_N=20 \text{ N}$, it is the $N(d_p)$ in the size range $d_p > 8 \mu\text{m}$ that increases whereas for the size range $< 8 \mu\text{m}$, it decreases.

6.6.3.1.2 Aerosol particles, $N_{air}(d_p)$

In figure 6.14 (a), the simulation of the size distribution of $N_{air}(d_p)$ is shown as a function of m . The curves with constantly decreasing peaks (or maximum aerosol particles number) and increasing size mode can be seen. In case of the total input force, F_{in} , the size distribution curves have an increasing size mode with increasing maximum particles number (figure 6.14 (b)). The $N_{air}(d_p)$ for $d_p \leq 100$ nm is continuously decreasing with increasing F_{in} .

A direct effect of σ on the size distribution of $N_{air}(d_p)$ can be observed in the figure 6.14 (c) where increasing σ leads to decreasing maximum number in $N_{air}(d_p)$ size distribution. In figure 6.14 (d) and (e) the total $N_{air}(d_p)$ (i.e. total number of aerosol particles lying in the size range of 20 nm to 20 μ m) is shown as a function of r_1 and ψ respectively. Both parameters have a positive correlation with total $N_{air}(d_p)$. The E_l , t_{imp} , K_c and H have a negative correlation with total $N_{air}(d_p)$ as shown in figure 6.14 (f), (g), (h) and (i) respectively. For a particle size range of 20 nm to 20 μ m, an increasing total $N_{air}(d_p)$ can be observed with increasing F_N when $F_N \leq 12$ N (or $(F_N)_{cr}$). Beyond this limit, the total $N_{air}(d_p)$ starts decreasing (figure 6.14 (j)). If this size range is divided in two sub size ranges i.e. 20 to 500 nm and 0.5 to 20 μ m, one may see that the aforementioned observation continues for the former case. However, in the latter case, total $N_{air}(d_p)$ saturates as soon as $F_N \geq 12$ N after initially increasing. This is exactly the same behavior observed experimentally in of the works [6.11] where a similar brick sample was subjected to the abrasion in same conditions and resultant aerosol emission was quantified using SMPS and APS.



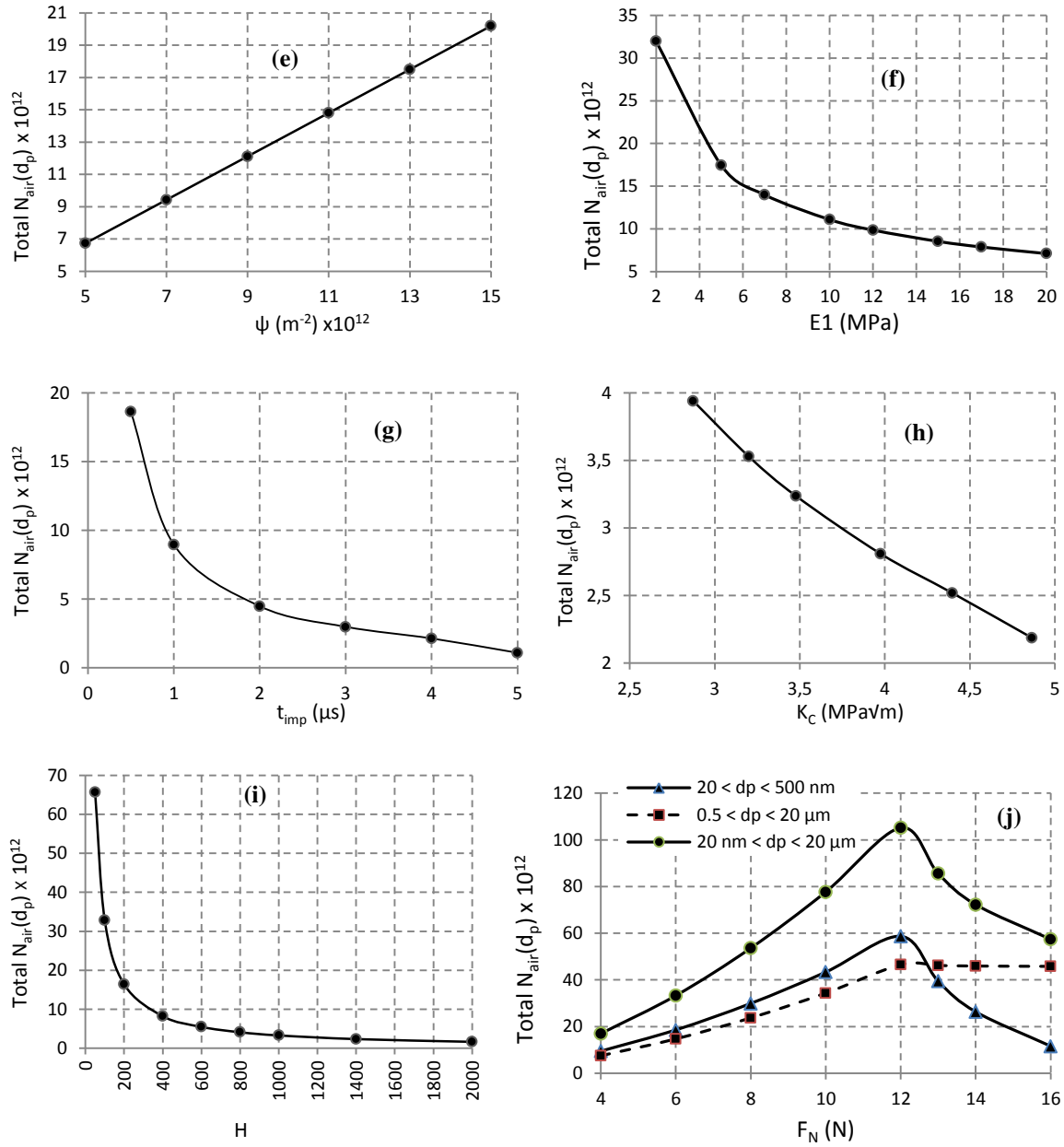


Figure 6.14: Effect of (a) m (b) Total input force acting during abrasion (c) standard deviation in asperity height distribution on aerosolized particles size distribution
Effect of (d) rms radius of the surface asperities (e) asperity number density (f) Young's modulus of the sample surface (g) impact duration (h) fracture toughness (i) hardness of the sample surface (j) normal force on the total number of aerosol particles generated during the abrasion of brick (determined using equation 34)

6.6.3.2 Wood

6.6.3.2.1 Wear debris particles $N(d_p)$

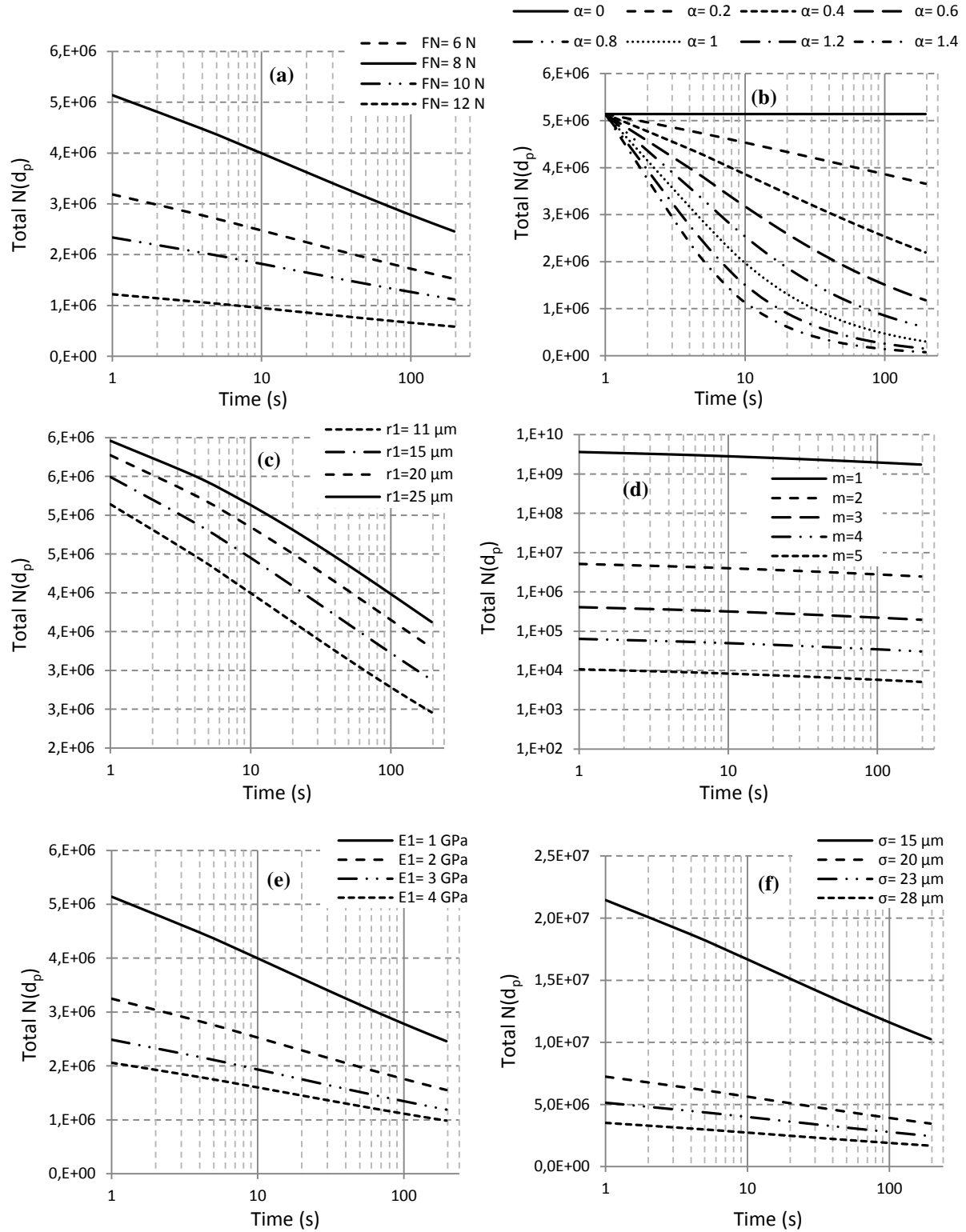
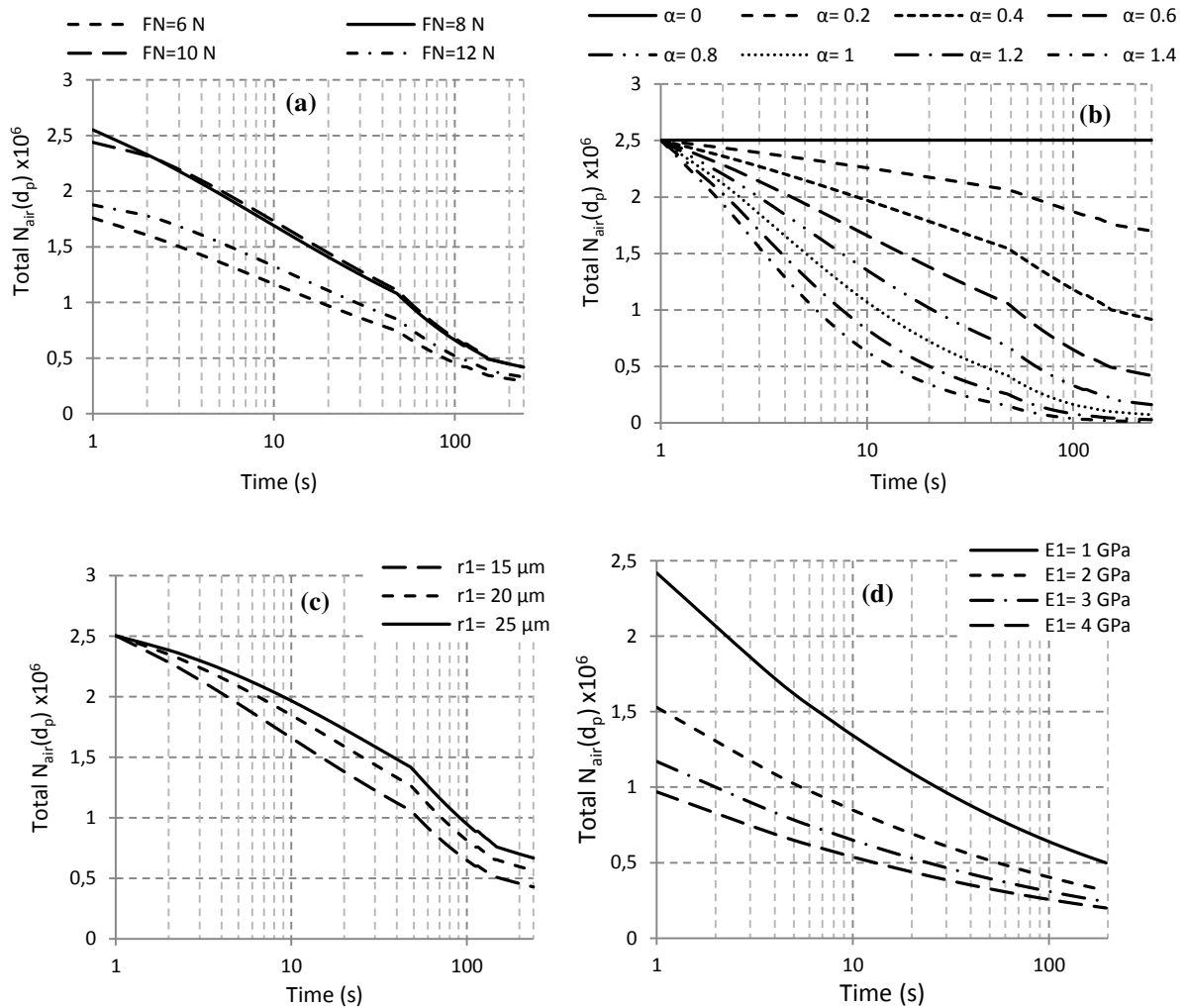


Figure 6.15: Effect of (a) m (b) rms radius of the surface asperities (c) normal force (d) surface porosity measure (e) young's modulus (f) standard deviation in the surface asperity heights distribution on the total number of wear particles generated during the abrasion of wood (determined using equation 15)

In figure 6.15 (a), the effect of the increasing F_N on the variation of the total $N(d_p)$, over the abrasion duration, t , is simulated for the wood sample. The effect of $(F_N)_{cr} = 8$ N on the total $N(d_p)$ can be observed as when $F_N \leq (F_N)_{cr}$, the total $N(d_p)$ increases with the increase in F_N but for $F_N > (F_N)_{cr}$, it decreases. The effect of the matrix porosity on the total $N(d_p)$ can be observed in figure 6.15 (b) where the total $N(d_p)$ is plotted as a function of α . For a nonporous matrix or $\alpha = 0$, a time independent total $N(d_p)$ can be observed. The total $N(d_p)$ does not only decrease with time but also with the value of α . With the increase in r_I , the total $N(d_p)$ increases (figure 6.15 (c)). In figure 6.15 (d), (e) and (f), one may observe that the total $N(d_p)$ decreases with increasing m , E_I and σ respectively.

6.6.3.2.2 Aerosol particles, $N_{air}(d_p)$

In figure 6.16, total $N_{air}(d_p)$ is plotted as a function of different parameters. The observations in this figure are almost similar to the ones in the figure 6.15.



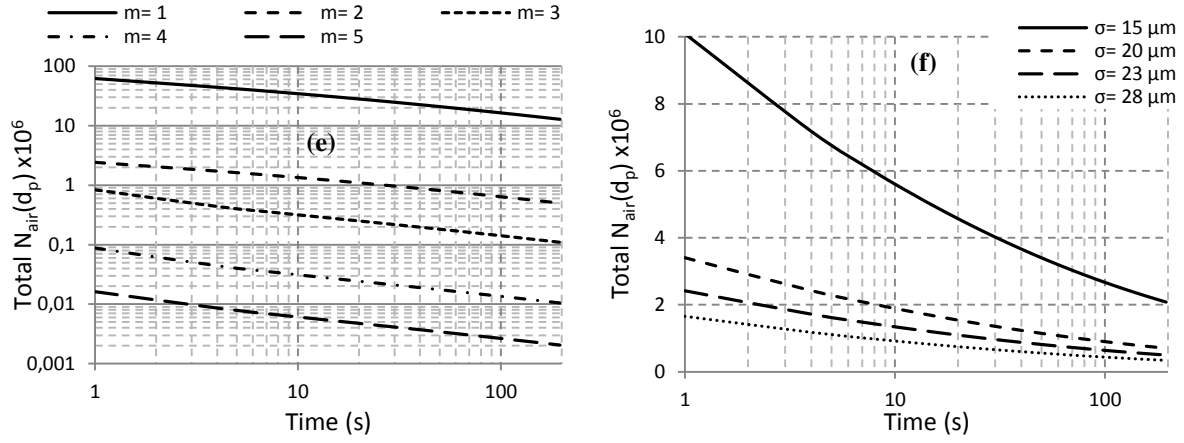
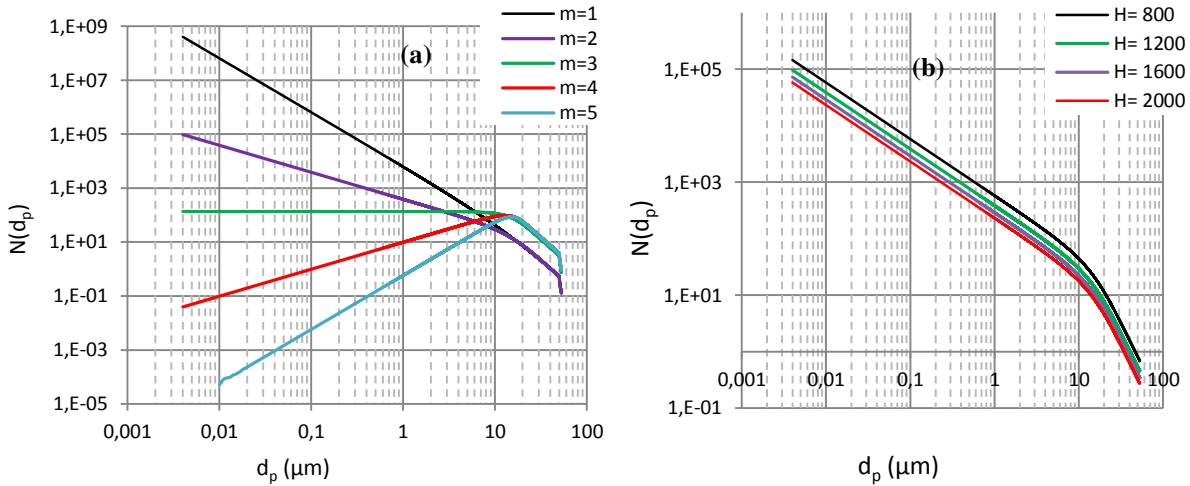


Figure 6.16: Effect of (a) normal force (b) surface porosity measure (c) rms radius of the surface asperities (d) young's modulus (e) m (f) standard deviation in the surface asperity heights distribution on the total number of aerosol particles generated during the abrasion of wood (determined using equation 34)

6.6.3.3 Stainless steel

6.6.3.3.1 Wear debris particles, $N(d_p)$

In figure 6.17 (a), the effect of the variation of m on the size distribution of $N(d_p)$, over a particle size range of 4 nm to 35 μm , is simulated. As the value of m changes from 1 to 2, $N(d_p)$ decreases for $d_p \leq 20 \mu m$. But unlike brick, it rests same for $d_p > 20 \mu m$. With $m=3$, $N(d_p)$ for $d_p \leq 20 \mu m$ again decreases but it starts increasing for $d_p > 20 \mu m$. Following the same pattern as that of brick, for $m=4$ and 5, $N(d_p)$ keeps on decreasing for $d_p \leq 20 \mu m$ but it remains almost constant for the size range $> 20 \mu m$.



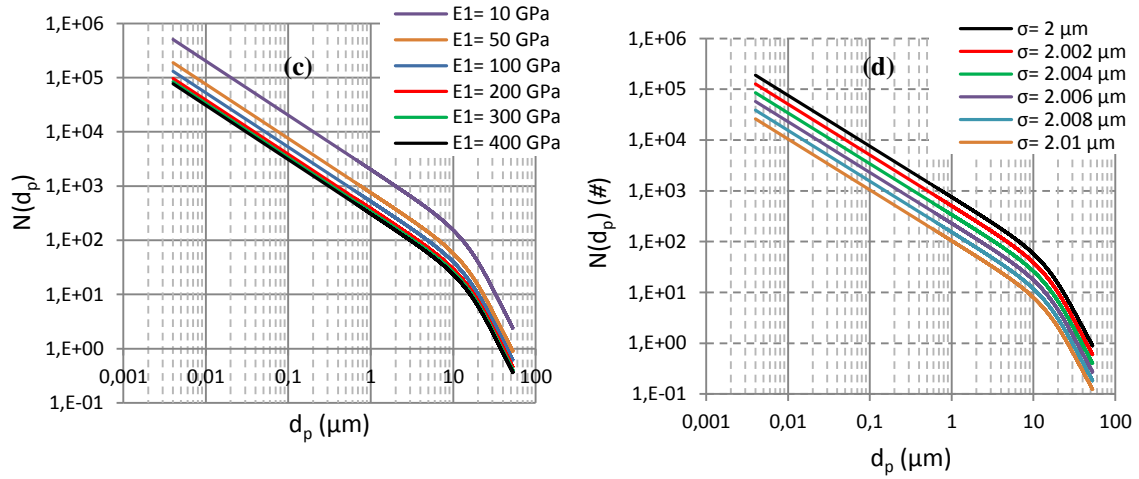


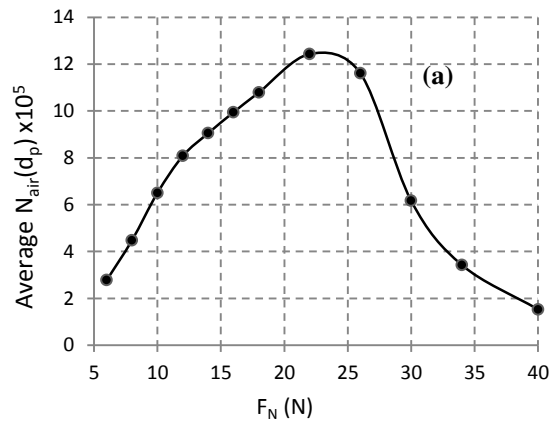
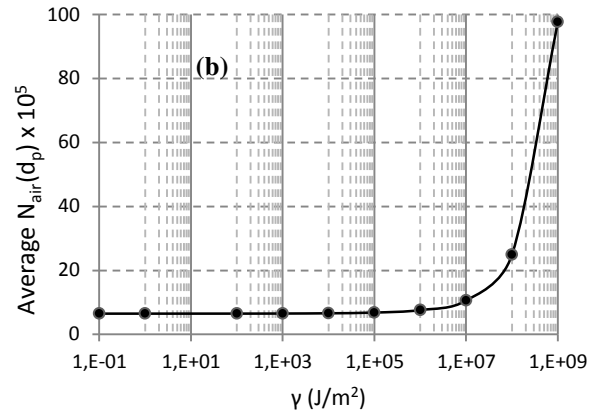
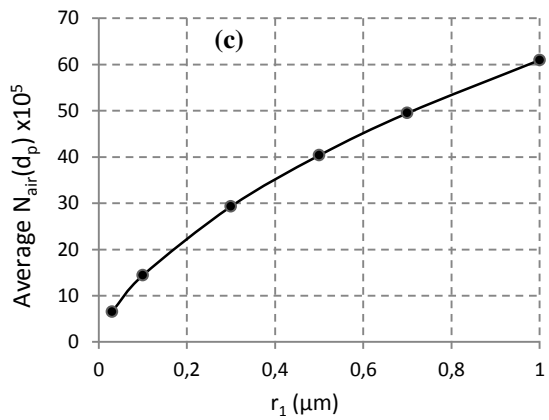
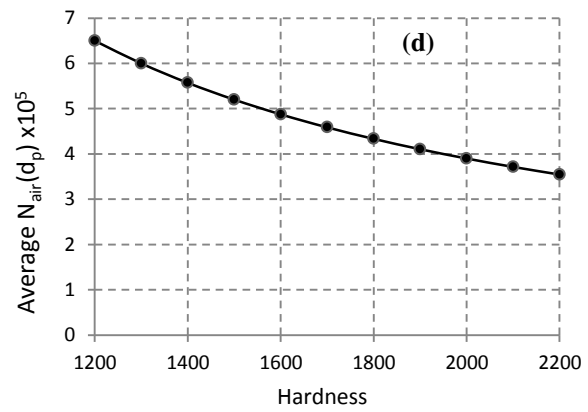
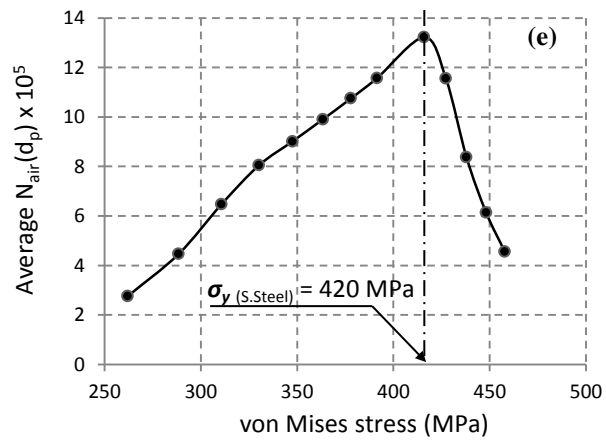
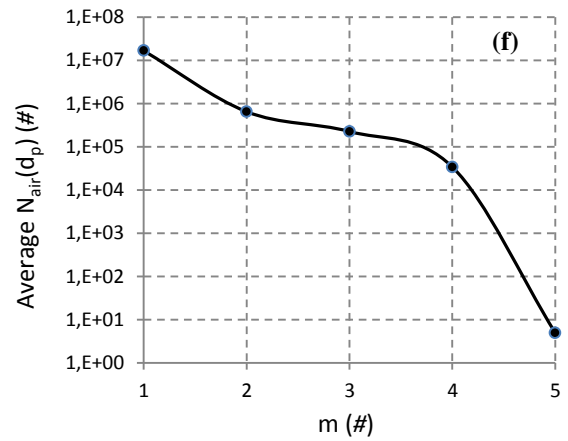
Figure 6.17: Effect of (a) m (b) surface hardness (c) sample surface Young's Modulus (d) std. dev. in the sample surface asperity heights distribution on the number-size distribution of the wear particles generated during the abrasion of s.steel (determined using equation 15)

Such behavior of m is comparable to another experimental study [6.42], also shown in figure 6.5, which measures the changes in wear particles size distributions as running hours accumulate during the abrasion of another steel sample. When the H , E_1 and σ increase, $N(d_p)$ decreases, as observed in the figure 6.17 (b), (c) and (d) respectively.

6.6.3.3.2 Aerosol particles, $N_{air}(d_p)$

In figure 6.18 (a), the effect of F_N on the average $N_{air}(d_p)$ is simulated. Since $(F_N)_{cr}$ for the steel sample is equal to 25 N, therefore, for $F_N \leq 25$ N, the average $N_{air}(d_p)$ increases with increasing F_N . For $F_N > 25$ N, it decreases. The role of surface energy, in the case of a chemically treated stainless steel like surface, is important which is shown in the figure 6.18 (b). For its lower values, the average $N_{air}(d_p)$ appears to be independent of it but when it starts approaching a value as high as 10^5 J/m^2 , there is an *abrupt* increase in the average $N_{air}(d_p)$.

By increasing r_1 and H , the average $N_{air}(d_p)$ increases and decreases respectively as shown in figure 6.18 (c) and (d). In figure 6.18 (e), the role of von Mises yield criterion is shown. As long as the von Mises equivalent stress (σ_{eq}) is smaller than the yield strength (σ_y) of the steel sample (420 MPa), the average $N_{air}(d_p)$ increases as the surface asperities haven't started yielding yet. But with the onset of yielding of the asperities ($\sigma_{eq} > \sigma_y$), the average $N_{air}(d_p)$ starts decreasing. The effect of m on the average $N_{air}(d_p)$ is shown in the figure 6.18 (f). As observed in the cases of brick and wood, the steel also has a decreasing average $N_{air}(d_p)$ with increasing m . Both E_1 and σ have a negative correlation with the average $N_{air}(d_p)$, as shown in figure 6.18 (g) and (h).



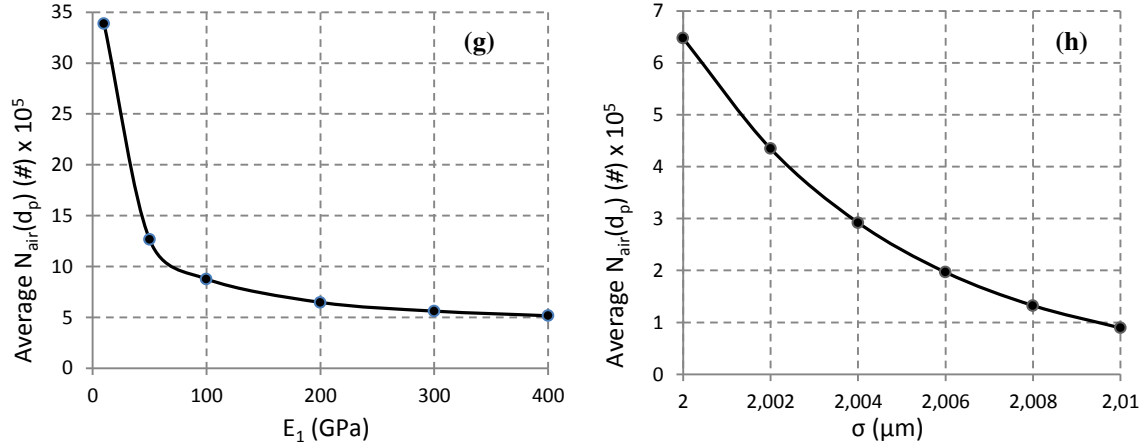


Figure 6.18: Effect of (a) normal force (b) surface energy (c) surface asperities rms radius (d) surface hardness (e) von Mises stress ($= F_{eq}/A_c$) (f) m (g) young's modulus (h) standard deviation in asperity heights distribution on the average number of aerosol particles generated during the abrasion of s. steel (determined using equation 34)

6.6.4 Model sensitivity analysis

To determine the relative sensitivity of the present aerosol emission model with respect to the different parameters, tornado charts are drawn for all three materials (figure 6.19 (a), (b), (c)) by varying the values of the material and process parameters enlisted in the tables 6.1 and 6.2. Both positive and negative changes of 25% are made in the magnitude of each parameter to observe the change in the emission output. The numerical values of the parameter, obtained after changes are also shown in the figures. All the parameters are listed vertically and they are ordered in such a way that the parameter to which the model is most sensitive appears at the top of the chart, the second most sensitive appears second from the top, and so on. Clearly, the order in which these parameters affect the emission is not same for the three materials. It is completely material type dependent.

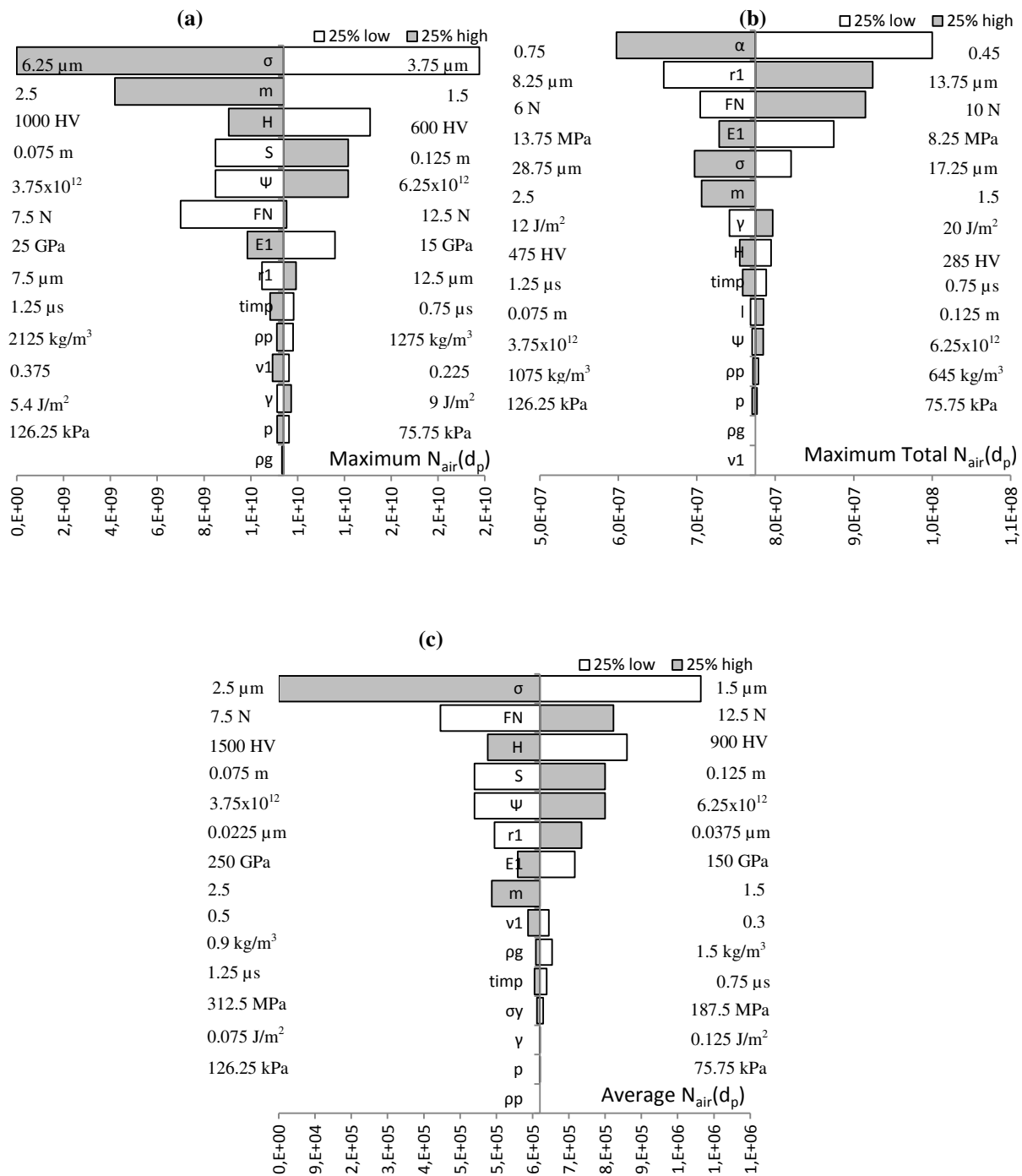


Figure 6.19: Relative sensitivity of the aerosol emission model with respect to different parameters for (a) brick (b) wood (c) steel sample

6.7 Discussion & Conclusions

In the present work, an effort has been made to develop a first generation predictive analytical model which, in association with the prior studies [6.11, 6.28], identifies the release mechanisms of the aerosol particles (i.e. the behavior of the asperities in response to the external loading) using microscopy techniques. Thanks to an original and multidisciplinary

approach that links different constitutive equations in Tribology, Material and Aerosol physics, it also quantifies the number of aerosol particles, thus resolving the inherent problem of the particle loss in conventional experimental tests of abrasion that are carried out for quantifying the released aerosol particles from a test material. Evidently, this is one of the first steps towards the theoretical quantification of the aerosol particles of such nature. The materials for which this model has been tested are brick, wood and stainless steel. During the course of the model testing and its simulation, it has been constantly noted that the aerosol particles emission is completely material type dependent. Other key findings with their discussions are enumerated below.

6.7.1 Most sensitive key parameters

As far as the sensitivity of these parameters is concerned, we found that the parameters to which $N_{air}(d_p)$ appears to be most sensitive are σ for the brick and steel samples and α for the wood sample. The parameter σ is a direct measure of the number of microscopic contacts between the sample surface asperities and the abrasive grains. These microscopic contacts are also sometimes called *load carrying micro-welds*. Higher the value of σ , lower is the number of contacts. This employs lower material removal and hence lower value of $N_{air}(d_p)$.

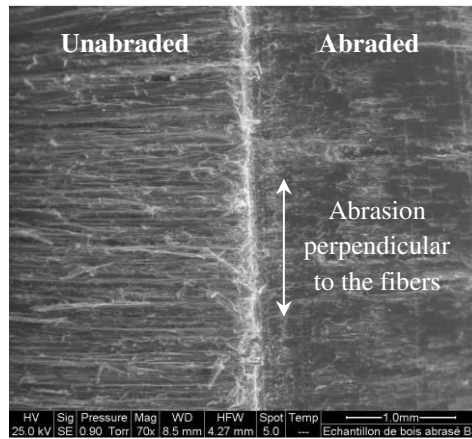


Figure 6.20: Scanning electron microscope image of the abrased and unabrased parts of the wood sample

For wood, the presence of pores proves to be very crucial. In figure 6.20, a microscopic image, showing both unabrased (on the left) and abrased parts (on the right) of the present wood sample, is shown. One may see that the unabrased part consists of fibers and pores (underneath and adjacent to the fibers). During abrasion in a direction perpendicular to these fibers, the material removal was observed to be the breaking of these fibers and getting displaced. It is believed that with the applied force via the abradant, the broken fibers start to get pushed and accumulated inside the pores. This is confirmed from the microscopic image of the abrased part of the wood which appears to be more planar and has lesser pores than its unabrased counterpart. In such a situation, only those particles aerosolize which do not get accumulated inside the pores. Hence, one may say that higher the porosity of a surface, lower is its tendency to generate the aerosol particles. This evolution in the surface conditions also has an impact on F_T which also evolves with the abrasion duration (t). As a result, its value is shown to be dependent upon t in the table 6.1.

6.7.2 Role of F_N

The aerosolization of the wear particles appeared to favor intermediate values of F_N i.e. when $F_N \approx (F_N)_{cr}$. This result is in accordance with one of our previous experimental studies [6.11] in which the role of F_N was investigated on a brick as a test sample.

6.7.3 Minimization of the emission

In the section 6.6.3, we saw the variation of $N_{air}(d_p)$ with respect to some of the identified material key parameters for all three materials. $N_{air}(d_p)$ was observed to follow the suit of increasing with some while for the others it was contrary. In table 6.5, we summarize the tendencies of these parameters to favor in order to minimize $N_{air}(d_p)$.

For a minimum $N_{air}(d_p)$, material parameters to	
maximize	minimize
Aerosol particle density (ρ_p)	Archard wear constant (K)
Surface hardness (H)	Surface asperities number density (ψ)
Surface Young's modulus (E_I)	Surface roughness (z_m, z_{max})
Poisson's ratio (ν_I)	Surface asperities' rms radius (r_I)
Atmospheric pressure (p)	Soild surface tension (γ)
Std. deviation in the asperity heights distribution (σ)	Pre-existing crack lengths in the surface asperities (l)
Air density (ρ_g)	-
Porosity index (α)	-
Surface yield strength (σ_v)	-

Table 6.5: Adjustment of the identified material key parameters to obtain a minimum emission

6.8 References

- [6.1] M. Vorbau, L. Hillemann, and M. Stintz, Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings, Journal of Aerosol Science 40, 209–217, 2009
- [6.2] N. Shandilya, O. le Bihan, M. Morgeneyer, A review on the study of the generation of (nano) particles aerosols during the mechanical solicitation of materials, Journal of Nanomaterials, Article ID 289108, 2014
- [6.3] D. Göhler, M. Stintz, L. Hillemann, and M. Vorbau, Characterization of nanoparticle release from surface coatings by the simulation of a sanding process, Annals of Occupational Hygiene 54, 615–624, 2010
- [6.4] O. Le Bihan, N. Shandilya, L. Gheerardyn, O. Guillon, E. Dore, M. Morgeneyer, Investigation of the release of particles from a nanocoated product, Advances in Nanoparticles, 2, 39–44, 2013
- [6.5] Petkovic, J., Zegura, B., Stevanovic, M., Drnovsek, N., Uskokovic, D. & Novak S. DNA damage and alterations in expression of DNA damage responsive genes induced by TiO₂ nanoparticles in human hepatoma HepG2 cells. Nanotoxicology 5, 341-53 (2011)
- [6.6] Unnithan, J., Rehman, M.U., Ahmad, F.J. & Samim, M. Aqueous Synthesis and Concentration-Dependent dermal toxicity of TiO₂ nanoparticles in wistar rats. Biological Trace Element Research 143, 1682-94 (2011)

- [6.7] Warheit, D.B., Brock, W.J., Lee, K.P., Webb, T.R. & Reed K.L. Comparative pulmonary toxicity inhalation and instillation studies with different TiO₂ particle formulations. *Toxicology Science* 88, 514–524 (2005)
- [6.8] Yamashita, K., Yoshioka, Y., Higashisaka, K. *et al.* Silica and titanium dioxide nanoparticles cause pregnancy complications in mice. *Nature Nanotechnology* 6, 321–328 (2011)
- [6.9] Barnard, A.S. One-to-one comparison of sunscreen efficacy, aesthetics and potential nanotoxicity. *Nature Nanotechnology* 5, 271–274 (2010)
- [6.10] Auffan, M., Rose, J., Bottero, J.Y. *et al.* Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective. *Nature Nanotechnology* 4, 634–641 (2009)
- [6.11] Shandilya N., Le Bihan O., Morgeneyer M., Effect of the Normal Load on the Release of Aerosol Wear Particles During Abrasion, *Tribol Lett* (2014) 55:227–234
- [6.12] Kapoor A., Williams J.A., Johnson K.L., The steady state sliding of rough surfaces, *Wear* 175, 81–92, 1994
- [6.13] Jiang J., Sheng F., Ren F., Modeling of two-body abrasive wear under multiple contact conditions, *Wear* 217, 35–45, 1998
- [6.14] Jeng Y.R. and Gao C.C., Changes of surface topographies during wear of surfaces with different height distributions, *Tribology Transactions* 43, 749–757, 2000
- [6.15] U. Olofsson, L. Olander, A. Jansson, Towards a model for the number of airborne particles generated from a sliding contact, *Wear* 267 (2009) 2252–2256
- [6.16] W. Cheng, K. Farhang, A contact model of nominally flat rough surfaces based on a visco-elasto-adhesive interaction, *Journal of Tribology*, 131, 044504-1 – 044504-2, 2009
- [6.17] F. Robbe-Valloire, B. Paffoni, R. Progrid, Load Transmission by elastic, elasto-plastic or fully plastic deformation of rough interface asperities, *Mechanics of Materials*, 33, 617–633, 2001
- [6.18] Kulkarni P., Baron P.A., Willeke K., *Aerosol Measurement: Principle, Techniques and Applications*, Third Ed., Wiley, Hoboken, New Jersey, United States, 2011
- [6.19] Brown W.K., Wohletz, Derivation of the Weibull distribution based on physical principles and its connection to the Rosin-Rammler and lognormal distributions, *J. Applied Physics*, 78, 2758–2763, 1995.
- [6.20] Bergstorm B.H., Sollenberger C.L., Kinetic energy effect in single particle crushing, *Transactions of the AIME* 220, 373– 379, 1961
- [6.21] Beall C., *Masonry Design and Detailing: For Architects Engineers, and Contractor*, McGraw Hill Text, 1997
- [6.22] http://www.engineeringtoolbox.com/young-modulus-d_417.html
- [6.23] Meyers M.A., Chawla K.K., *Mechanical Behavior of Materials*, Prentice Hall Inc., 1999
- [6.24] <http://workshoppages.com/WS/Misc/Wood-Hardness-Chart.pdf>
- [6.25] Callister W.D., *Materials Science and Engineering: An Introduction*, 3rd Edition, John Wiley & Sons, Inc. New York
- [6.26] http://cfppah.free.fr/docs/Table_des_masses_volumiques.pdf
- [6.27] Kinloch A.J., *Adhesion & Adhesives - Science & Technology*, Chapman & Hall, London, 1987
- [6.28] Morgeneyer, M., Shandilya, N., Chen, Y.M. & Le Bihan, O. Use of a modified Taber abrasion apparatus for investigating the complete stress state during abrasion and in-process wear particle aerosol generation. *Chem. Engg. Res. & Design* (2014) doi: <http://dx.doi.org/10.1016/j.cherd.2014.04.029>

- [6.29] ASTM. International. Standard Test method for the abrasion of organic coatings by the Taber Abradant. ASTM D4060 (2007)
- [6.30] ASTM. International. Standard Test Methods for Dry Abrasion Mar Resistance of High Gloss Coatings. ASTM D6037 (1996)
- [6.31] ASTM. International, Standard Test Method for Resistance of Transparent Plastics to Surface Abrasion ASTM D1044, (2008)
- [6.32] <http://accuratus.com/pdf/sicprops.pdf>
- [6.33] Morgeneyer, M., Le Bihan, O., Ustache, A. & Aguerre-Chariol, O. Experimental study of the aerosolization of fine alumina particles from bulk by a vortex shaker. *Powder Technology* 246, 583–589 (2013).
- [6.34] Le Bihan, O., Morgeneyer, M., Shandilya, N., Aguerre Chariol, O. & Bressot, C. Handbook of Nanosafety- Measurement, Exposure and Toxicology. In: Vogel, U., Savolainen, K., Wu, Q., Van Tongeren, M., Brouwer, D., Berges, M. (eds.) *Emission Chambers- A method for nanosafety*, Ch. 7 (Academic Press, Elsevier Inc., San Diego, 2014)
- [6.35] Williams J.A., Wear modelling: analytical, computational and mapping: a continuum mechanics approach, *Wear* 225–229 1999 1–17
- [6.36] Tabor D., Surface forces and surface interactions, *J. Colloid Interface Sci.* 58, 2-13, 1977
- [6.37] Johnson K.L., Kendall K., Roberts A.D., *Surface energy and the contact of elastic solids*, *Proc. R. Soc. Lond. A.* 324, 301-313, 1971
- [6.38] Derjaguin B. V., Muller V. M., Toporov, Y.P., Effect of Contact Deformations on the Adhesion of Particles, *J. Colloid Interface Sci.* 53, 314-326, 1975
- [6.39] Rabinovich Y.I., Adler J. J., Ata A., Singh R.K., Moudgil B.M., Adhesion between Nanoscale Rough Surfaces II: Measurement and Comparison with Theory, *Journal of Colloid and Interface Science* 232, 17–24 (2000)
- [6.40] Rosin P., Rammler E., The Laws Governing the fineness of Powdered Coal, *Journal of the Institute of Fuel* 7, 29–36, 1933
- [6.41] Williams P.A., Clarke I.C., Understanding polyethylene wear mechanisms by modeling of debris size distributions, *Wear* 267, 646-652, 2009
- [6.42] Lockwood, F.F. and Dally (1992), *Lubricant Analysis*, 18th edition, Metals Handbook, Tribology, ASM, 19, 300-312
- [6.43] Callister W.D., *Materials Science and Engineering: An Introduction*, 3rd Edition, John Wiley & Sons, Inc. New York, 1994
- [6.44] Tabor D., Friction, lubrication and wear, in Matijevic E. (Ed), *Surface and Colloids Science*, vol. 5, John Wiley, 245-312, 1972

7. DISCUSSION AND CONCLUSIONS

For the present thesis, the ultimate goal is to contribute in the process of designing the products which are low emissive with respect to ENM or “nanosafe by design”. For this, an approach is favored which is not only capable of understanding and identifying the ENM release mechanisms, but can also predict their quantity of emission and compare them without carrying out the real tests for each type of ENM.

The understanding of the emission phenomenon was developed on the basis of the literature review and the results from the preliminary abrasion tests of the traditional products and their characterization. Based on this understanding, a set of key parameters were identified which are believed to play a key role during emission. This set contains both material parameters (or material properties) and process parameters (or properties of the applied abrasion process). Through an analytical model and our prior understanding of the emission phenomenon, definite relations of these key parameters with the emission were also identified so that they can be manipulated in a way that the emission can be minimized.

Three case studies were also done on two different commercial nanostructured products- a brick reinforced with nanoparticles and photocatalytic nanocoatings. These case studies have further helped us in understanding the nature of the ENM emission. In other words, it helped us to understand that whether the ENM gets emitted in the form of the aerosols composed of ENM embedded in the product matrix or the aerosols composed of free ENM with no matrix and a high specific surface area.

Now, the purpose of this particular section is to summarize and discuss the conclusions vis-à-vis the aims which were originally defined for this thesis. This shall also help in proposing the perspective for the thesis.

7.1 Development of an experimental set-up capable of simulating real life stresses in the laboratory

A Taber[®] 5750 linear abraser has been chosen for the thesis study and modified instrumentally by mounting a strain gauge on a horizontally displacing replicated aluminum alloy bar (section 4). This modification has allowed us to simulate and measure the stresses to which a particular product is subjected to real life of its use in our experimental set-up. The pre-requisite for such a simulation had been the knowledge of the magnitude of the normal and tangential stresses acting during a particular real life activity. In the original standard form of this Taber[®] 5750 linear abraser, only the magnitude of the normal stress is known and controlled. But the modified form of this abraser can also measure the tangential force, thus making the simulation of the real life stresses possible.

7.2 Key parameters during particles emission

Thanks to an extensive scientific literature review and various preliminary experimental studies, we were able to define a total of 18 process and material parameters that are considered to play a key role during aerosol particles emission (section 3). On one hand, the process key parameters include Normal force, Tangential force, Abrasion speed, Air density and Atmospheric pressure. On the other hand, the material key parameters include Surface

hardness, Surface asperities' rms radius, Surface roughness, Solid surface tension, Surface asperities' number density, Surface young's modulus, Surface Poisson's ratio, Std. deviation in the asperity heights distribution, Surface yield strength, Aerosol particle density, Surface porosity and Pre-existing crack lengths in the surface asperities. Each parameter has its own degree of correlation with the emission and relative importance with respect to each other.

7.3 Particles emission mechanism

The particles emission mechanism is a direct result of the removal mechanism of the surface asperities during abrasion. In other words, the shape, size and the number of the aerosol particles emitted during abrasion depends upon the type of the surface asperities removal mechanism which can be fracturing, ploughing, abrasion wear and uprooting. It was found that depending upon the type of the material (defined by the material key parameters) and stress applied (defined by the process key parameters), these removal mechanisms are decided.

Among the process key parameters, the two most important ones identified are Normal and Tangential forces. In conjunction with different types of materials, they decide the type of abrasion i.e. light (i.e. $F_N < (F_N)_{cr}$), mild (i.e. $F_N \approx (F_N)_{cr}$) or severe (i.e. $F_N > (F_N)_{cr}$). If two materials, having different material properties, are abraded with same values of these two forces, it is highly probable that they might have two different kinds of abrasion and different quantities of the particle emission. Therefore, the maximum value of these two forces that can be applied under each type of abrasion is difficult to precise.

During various tests, carried out on the materials including brick, wood, steel, polymer and ceramics, it is constantly observed that the number of the aerosol particles, in general, is favored by mild abrasion conditions (i.e. $F_N \approx (F_N)_{cr}$). In other words, under mild abrasion conditions, majority of the aerosols are composed of the particles that have a nano or sub micronic size and their number concentration is relatively high. Under light abrasion conditions, majority of the aerosols is also composed of the particles that have a nano or sub micronic size but their number concentration is relatively low. Under severe abrasion conditions, majority of the aerosols is composed of the microparticles and their number concentration is comparable to that obtained during intermediate abrasion conditions. In the same case, there is a general tendency of the aerosol particles to eventually deposit back to the surface rather than to remain aerosolized or suspended in air for long time.

7.4 Effect of mechanical stresses and environmental weathering couple on the nanostructured products

The results from the case study, carried out to test the effect of applying the mechanical stresses alone on a nanocoating (section 5.2), revealed that the emitted ENM are never in their pristine form, but rather embedded inside the dispersant matrix of the nanocoating. Based on the results, we also conclude that one may achieve the reduction in the ENM release from the nanocoatings by following either of the two or both remedies:

1. Selection of a product having good interfacial adhesion with the substrate
2. Increase in the number of coating layers on the substrate

A coating on the surface is believed to act like a resistor to the externally applied mechanical stress which reduces its net impact. By increasing the number of the coating layers, the

resistance effect further improves. Also, the surface energy (one of the key parameters identified among other 20 key parameters), lowers with increasing number of the layers. Since, the surface energy is observed to be directly proportional to the number of the released particles, therefore, its lowering leads to the lowering in the emission.

The environmental weathering- a phenomenon that may have a strong effect on the changes in the material properties due to its exposure to UV rays, humidity and heat- is also observed to play an important role in deciding the nature and number of the released ENM. In the literature, the environmental weathering is known to bring degradation of the matrix. However, the extent of this degradation depends upon the type of the matrix and the duration of the weathering. During the course of the experiments, it is constantly observed that the occurrence of the ENM inside a matrix, during emission, continues until the matrix has a high interfacial shear strength value. With increasing weathering duration, there is a step-wise structural deterioration of the nanocoating which leads to the decrease in the interfacial shear strength between the matrix and the ENM. As a result, the emission of free ENM starts occurring. In such a case, if there is a flow of water over the surface, known as *runoff*, the leaching of these ENM in the runoff water is highly probable. With a high specific surface area, these free ENM now accentuate a potential risk in terms of nano-toxicity.

One of the *Unique Selling Propositions* of our approach in studying this aspect of emission is that it focuses on finding a weathering duration threshold beyond which the chosen nanocoating is no longer useful, i.e. nanocoating's useful life. In the present case, it's 4 months of accelerated weathering. This is done through a continuous monitoring of the in-process nanocoating state which allowed us to note the exact duration in which the nanocoating started to degrade. This is the feature which distinguishes it from other similar scientific studies as they deal with the concept of the environmental weathering by applying it on a test sample for a predetermined duration with no in-process monitoring of the ongoing weathering.

Another important aspect of the weathering tests with which the researchers are confronted to is that the continuation of the weathering tests to its final limits is a time consuming and expensive process. It generally continues for several months and a lot of preparations are required to ensure the test continues in standard conditions. In order to tackle with such problems, three indicators, namely, *Emission Transition Pace* (ETP), *Stable Emission Level* (SEL) and *Stable Emission Duration* (SED) were presented and evaluated during the present thesis. The aim of these indicators is to predict the complete time of failure of the nanocoatings and the potential increase of ENM release into the air from the results of short weathering durations. Thus, it replaces the use of prolonged weathering tests.

7.5 Analytical modeling of the particles emission

An analytical model, prepared during this thesis, aims to predict quantitatively the aerosol particles released during abrasion and categorize the key parameters in the hierarchy of their impact on the emission. This model is based on the experimental results obtained during various studies of three different material samples: brick, wood and stainless steel. Such an approach ensures the model covers a wide range of materials. If the number concentration of the aerosol particles is observed experimentally to be not constant with time or time varying size distributions (as observed in the materials in which the surface conditions evolve with every abrasion stroke), this model permits to simulate such variations too. The basic principle upon which this model is based says that the number of aerosol particles generated during

abrasion is a fraction of the total number of debris wear particles. This fraction is nothing but the aerosolization probability of the debris wear particles which, among other properties, primarily depends upon the particle size. If expressed mathematically, one may say that $N_{air}(d_p) = N(d_p) \cdot P(d_p)$. Here $N_{air}(d_p)$ is the number of aerosol particles, $N(d_p)$ is the number of debris wear particles, $P(d_p)$ is the aerosolization probability and d_p is the particle diameter or size. During the formulation of the number of wear particles, the Archard and Rosin-Rammler distribution laws play a vital role. The aerosolization probability is considered to be the net resultant of four forces which act simultaneously on a debris wear particle- Gravitational force, Drag force, Diffusive force and Net mechanical input force. Out of these four forces, it is the mechanical input force that is considered to be a favorable one towards aerosolization of a particle. The rest are considered to be the opposing ones.

The model results reveal that the aerosolization of the wear particles is directly dependent upon the material parameters like surface hardness, roughness etc. When their sensitivity towards the emission is studied with respect to the process parameters like externally applied forces, abrasion speeds etc., they appear to be more sensitive than the process parameters. For the three tested materials- brick, stainless steel and wood, the standard deviation in the surface asperity heights distribution appears to be the most sensitive one for brick and stainless steel. For wood, it is its surface porosity. In accordance with the experimental results, the model simulation results show a positive correlation (i.e. tendency of the emission to increase with increase in the parameter's magnitude) of various parameters like surface roughness, energy, asperity/grain number density and abrasion speed with emission. However, the parameters like plasticity index, elastic moduli, hardness and fracture toughness of a material's surface appear to have a negative correlation (i.e. tendency of the emission to decrease with increase in the parameter's magnitude).

8. PERSPECTIVES

8.1 Improvement in the experimental set-up

A particular point has been consistently highlighted in the present manuscript- **Aerosol Particles loss** during their analysis. The aerosol particles, generated during abrasion, are prone to get lost prior to their analysis due to two probable reasons (i) deposition on the walls or the surfaces of the emission test chamber (ii) deposition inside the connecting tubes. As a result, their concentration, as shown by the particle sizers and counters, is somewhat lower than the actual value.

As shown in the research articles, some preliminary attempts have been made during the present thesis to account for the loss in the former case by carrying out time tracking analysis of the polydispersed NaCl aerosol particles using SMPS and CPC. The details on the latter case have already been provided in the section 5.1.

The results of these attempts have helped in evaluating the aerosol particles losses in our present experimental set-up but we didn't work on minimizing these losses. Therefore, we recommend that the future studies should be oriented towards an improvement in the particle transport efficiency from the emission test chamber (containing the abraser and test sample) to the particle sizers and counters by minimizing the losses occurring in between. This shall require some probable changes in the design of the emission test chamber like fluid flow inside the chamber. As a result, a complete quantitative analysis of the aerosol particles will become possible which is rather semi-quantitative for the moment.

8.2 Variation in the nanostructured products

The two types of the nanostructured products tested during this thesis were nanocoatings and nanoparticles reinforced brick. Moreover, the ENM used in these products was TiO₂ nanoparticles. As a result, we are not in a position to fully confirm any result which we got during our study of these products. In order to do so and further enhance the knowledge based upon the emission from different nanostructured products, a larger variety of both matrices (polymer, concrete and metal) as well as ENM (Ag, CeO₂, Au etc.) should be studied.

8.3 Improvement in the analytical model of emission

As mentioned earlier, the **Rosin-Rammler distribution** is conventionally used from micrometer to millimeter size range for the debris wear particles generated during comminution like processes. During the model development, one of the major assumptions undertaken is that the Rosin-Rammler distribution can approximate the **size distribution of the debris wear particles** in the nanometer size range too. However, no specific test was done to validate this assumption. Even though we have observed close agreement between the experimentally measured and theoretically calculated data in the figures 6.10, 6.11 and 6.12, specific experimental tests must be done in the future for measuring the size distribution of the **debris wear particles**. This may include ferrography tests for the ferrous products whereas liquid light diffusion analysis for the polymeric or masonry products.

The proposed values of t_{imp} , I , α and form of the semi-empirical relations of m , V_{wa} and V_{wd} (equations 10, 11, 13 and 14) were decided in such a way that the model results fit in a best way possible with the experimentally measured results of emission, as seen in figures 6.10,

6.11 and 6.12. However, their function is not to serve as the curve fitting parameter. One may deduce the final value of t_{imp} , and the form of the semi-empirical relations of m , V_{wa} and V_{wd} , once the aerosol particles losses are minimized, as suggested in the section 8.1.

Apart from this, the effect of **frictional heating and contact temperature** on the aerosolization of the wear particles is neglected here. Such an assumption holds well as long as the relative sliding velocity is not high enough. But, if that is not the case, the frictional heating may result into the localized melting of the surfaces and formation of a superficial layer, especially in the metals. It completely changes the contact conditions and thus may have a direct impact on the shape, size and chemical composition of the aerosol wear particles. Nevertheless, to our knowledge, no experimental work is present in the literature that has studied this effect.

It must be noted that the present model is not concerned with the **aerosol dynamics** in the air i.e. its behavior with other similar aerosol particles and the air molecules. The calculations have been done to the limit when an aerosol particle just leaves the surface. The aim for this model is to evaluate the aerosol particle emission tendency of a material when it is subjected to the mechanical solicitation in the form of its sliding abrasion. Therefore, the complex phenomena like aerosol nucleation, coagulation and their inter-particles interaction haven't been considered.

As pointed out in the section 6.5.1, the evaluation of the total wear volume (equation 9) is an **iterative calculation** which considers the successive changes occurring in the contact conditions with each abrasion stroke. Theoretically, the magnitude of the wear volume should decrease progressively with each stroke. However, for the sake of simplicity, we have approximated the total wear volume to the first term only in equation 9. Due to this, we are considering the wear volume to be same in all abrasion strokes. But, the most effective way would be to develop a numerical method which can carry out the iterations to calculate more exact values of the successively decreasing wear volumes.

As it is clear, the present model hasn't been tested against the **heterogeneity** (i.e. distinct nonuniformity in the composition or character) and **anisotropy** (i.e. having properties that differ according to the direction of measurement and loading) of a test sample. Although, wood is known to exhibit natural anisotropic behavior, but we have carried out the abrasion tests in only one particular direction of the fibers orientation i.e. perpendicular to the fibers. Therefore, in order to make this model suitable for more advanced materials like fibers or nanotubes reinforced composites, effect of the parameters like external loading direction, fillers orientation, texture patterns etc. should also be considered.