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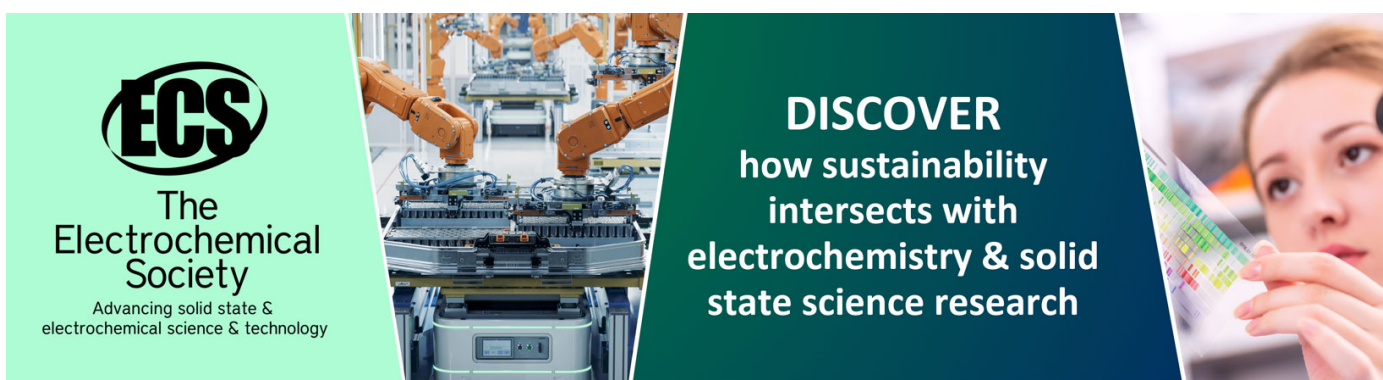
Development of a test method for protective gloves against nanoparticles in conditions simulating occupational use

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Development of a test method for protective gloves against nanoparticles in conditions simulating occupational use

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Abstract. Nanoparticle manufacture and use are in full expansion. The associated risks of occupational exposure raise large concerns due to their potential toxicity. Even if they stand as a last resort in the traditional occupational Health & Safety (H&S) risk management strategy, personal protective equipment (PPE) against nanoparticles are an absolute need in the context of precautionary principle advocated by H&S organizations worldwide. However no standard test method is currently available for evaluating the efficiency of PPE against nanoparticles, in particular in the case of gloves. A project is thus underway to develop a test method for measuring nanoparticle penetration through protective gloves in conditions simulating glove-nanoparticle occupational interaction.

The test setup includes an exposure and a sampling chamber separated by a circular glove sample. A system of cylinders is used to deform the sample while it is exposed to nanoparticles. The whole system is enclosed in a glove box to ensure the operator safety during assembly, dismounting and clean-up operations as well as during the tests. Appropriate nanoparticle detection techniques were also identified.

Results are reported here for commercial 15nm TiO₂ nanoparticles - powder and colloidal solutions in 1,2-propanediol, ethylene glycol and water - and four types of protective gloves: disposable nitrile and latex as well as unsupported neoprene and butyl rubber gloves. They show that mechanical deformations and contact with colloidal solution liquid carriers may affect glove materials. Preliminary results obtained with TiO₂ powder indicate a possible penetration of nanoparticles through gloves following mechanical deformations.

With the growing expansion of nanotechnologies worldwide, increasing risks of exposure to nanoparticles are expected. This is especially worrying in the case of occupational settings, where the level of toxicological risk has been evaluated as significant [1]. In the context of precautionary principle advocated by numerous H&S organizations around the world [2], large efforts are directed towards the development of standards [3], guides [4,5] and risk assessment and control methodologies [6] specific for nanomaterials. Indeed, it has been estimated that the number of workers involved in nano-related activities would reach 2 millions by 2015 [7]. As a result and even if they stand as a last resort in the traditional occupational H&S risk management strategy, PPE against nanoparticles are

needed right away [8]. Yet, knowledge, data and test methods in this area are scarce whereas questions have been raised about the efficiency of existing PPE products against nanoparticles [9].

If some progress has been accomplished regarding respiratory PPE against nanoparticles, the question of dermal protection is still largely unexplored [9]. However, studies are increasingly showing that skin is a possible uptake route for nanoparticles, either when injured by abrasion [10], after repeated flexions [11] or even intact [12]. Pores, hair follicles and sweat may also increase the likelihood of nanoparticles percutaneous transportation [13].

A limited number of groups have reported research carried out on protective clothing and gloves against nanoparticles. Most of it involves aerosols. In the case of air-permeable fabrics, tests have been performed with oleic acid, KCl, NaCl, graphite, TiO₂ and Pt nano-aerosols as small as 10nm in diameter [14-20]. According to some authors, the variation of the nanoparticle penetration ratio through fabrics as a function of the particle diameter and air flow rate is in agreement with the filtration theory [15,16,21]. Others have reported diverging results, for example a plateau in the penetration of graphite nanoparticles larger than 50 nm through woven cotton with a 0.6 cm/s face velocity [18], and a higher penetration of 30nm graphite nanoparticles through a paper fabric than 80nm ones [9]. A much higher efficiency against nanoparticle penetration was observed for a thin high-density polyethylene non-woven membrane than with other, thicker fabrics, with and without air flow [17-20]. In the case of protective gloves, the results seem conflicting. Diffusion of 30 and 80nm graphite nanoparticles through nitrile, vinyl, latex and neoprene commercial glove samples has been reported [17] while no penetration was later measured for the same gloves with 40nm graphite and 10nm TiO₂ and Pt particles [18,19]. These data involving nano-aerosols were obtained without air flow.

Exposure to nanoparticles in occupational settings may also involve powder and colloidal solutions. This situation is especially relevant to protective gloves. Scanning electron microscopy (SEM) observations of latex and nitrile rubber gloves after static and dynamic contact with clay and alumina powders have shown that nanoparticles tend to accumulate inside micrometer-size pores on the surface of the gloves [22]. In the case of nanoparticles in colloidal solutions, some concerns have been raised about increased risks related to the liquid carrier [23]. In addition, the mechanical deformations suffered by gloves in service as well as the presence of a microclimate inside the gloves may also affect the penetration of the nanoparticles. It is thus important that test methods take into account conditions experienced by PPE while in use [21].

This paper reports on the development of a test method for measuring nanoparticle penetration through protective gloves in conditions simulating glove occupational use. It describes the setup designed for the test as well as the nanoparticle detection techniques investigated. Finally, it provides preliminary results obtained with commercial 15nm TiO₂ powder and colloidal solutions, and four types of protective gloves: disposable nitrile and latex as well as unsupported neoprene and butyl rubber.

1. Materials

1.1. Nanoparticles

Titanium dioxide (TiO₂) nanoparticles have been selected for the development and validation of the test method since it is one of the most widely used nanomaterials [24]. TiO₂ powder (15 nm, 99.7% pure anatase) was obtained from Nanostructured & Amorphous Materials, Inc. (Houston, TX). A statistical analysis (n = 174) of transmission electron microscopy (TEM) pictures (JEOL JEM-2100F) of the bulk powder sprinkled on carbon-coated copper grids revealed the presence of aggregates and agglomerates (see Figure 1). As illustrated in Figure 2, the average size of aggregates is 100 nm and some agglomerates are as large as 1200 nm. In fact, only two individual nanoparticles were counted in the analysed sample. Figure 1 also shows the presence of rod-like rutile nanoparticles in addition to the spherical anatase. A 3 to 6% ratio of rutile in the TiO₂ powder was measured by X-ray diffraction (Philips X'PERT).

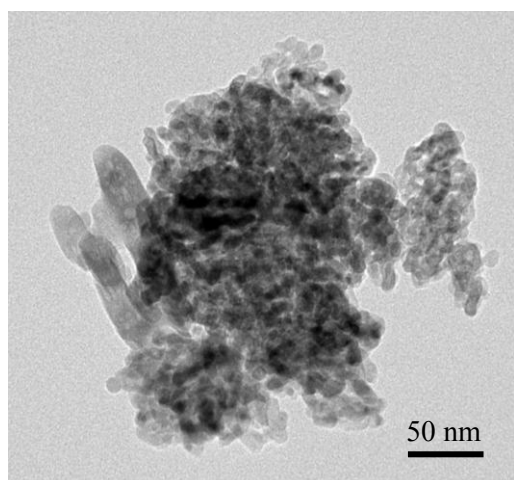


Figure 1. TEM image of the TiO₂ powder.

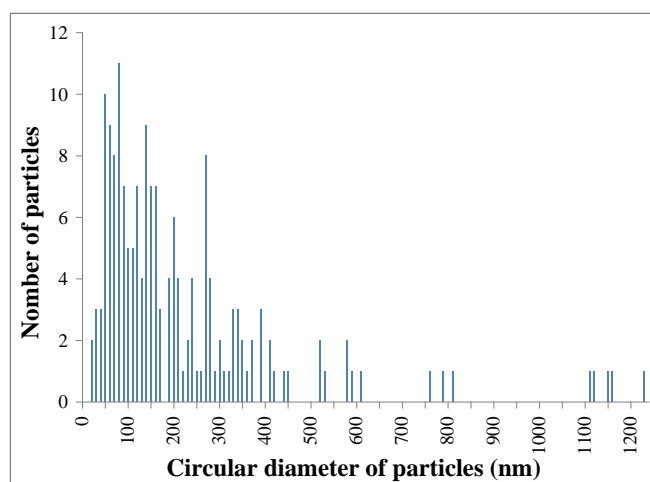


Figure 2. Size distribution of the TiO₂ powder.

TiO₂ colloidal solutions (15 nm, anatase) in water (15 wt%, Nanostructured & Amorphous Materials, Inc., Houston, TX), ethylene glycol (20 wt%, idem) and 1,2-propanediol (20 wt%, M K Impex, Mississauga, ON) were also obtained. Analysis of the colloidal solutions by fluorescence correlation spectroscopy (FCS) was performed and provided a particle size of 21 ± 2 nm for TiO₂ colloids in water and 35 ± 3 nm for TiO₂ colloids in ethylene glycol. It can be noted that no characterization of the TiO₂ colloidal solutions by microscopy was possible due to the formation of a μm -thick viscous film on the nanoparticles upon solvent evaporation. It was attributed to the presence of additives in the colloidal solutions, used for example as stabilising agents.

1.2. Gloves

Four types of protective gloves made of different elastomers were selected for the study: disposable nitrile rubber gloves (100 μm thick), disposable latex gloves (100 μm thick), non-supported neoprene gloves (450 μm thick) and non-supported butyl rubber gloves (700 μm thick). The samples were taken in the palm section of the gloves.

The external surface of the gloves, i.e. in contact with nanoparticles, was analyzed by SEM (Hitachi S3600N). Figure 3 displays examples of what was obtained for the nitrile (Figure 3.a) and neoprene (Figure 3.b) gloves. The surface of nitrile samples shows micrometer-size pores, in agreement with what has already been reported [22], while neoprene also includes the presence of cracks. In the case of latex and butyl rubber gloves, plate-like structures are observed.

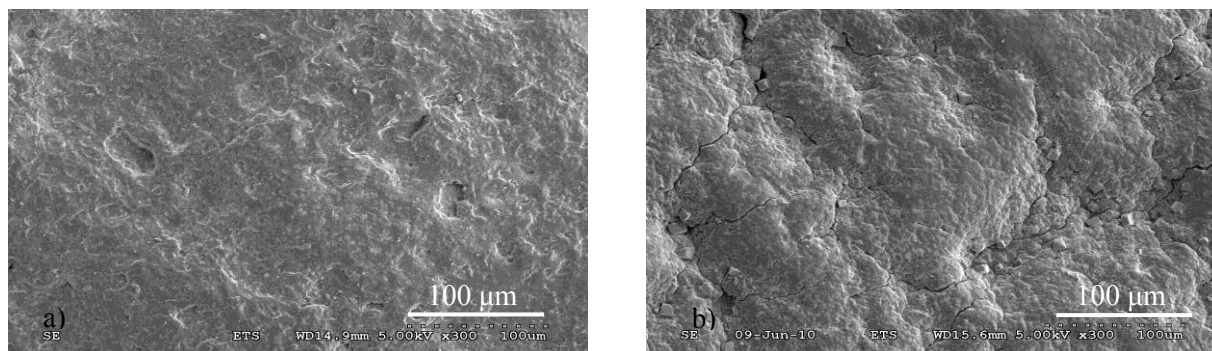


Figure 3. SEM pictures of external glove surface: a) nitrile and b) neoprene.

2. Design of the Test Setup

A setup has been designed to fulfill a series of requirements. They include the mode of application of the nanoparticles (powder and colloidal solutions), the simulation of glove use conditions (mechanical deformation, presence of a microclimate inside the glove), sampling outputs corresponding what is needed by nanoparticle detection techniques, as well as the safety of the operator.

As illustrated in Figure 4, the test setup comprises an exposure and a physiological/sampling chamber between which is secured a circular glove sample. Both chambers have a 50-mm inner diameter and a 60-mm inner height. All setup parts in contact with nanoparticles are made out of ultrahigh molecular weight polyethylene to limit the nanoparticle adsorption effect observed by FCS with other materials like anodized aluminum in the case of colloidal solutions. The nanoparticles are introduced in the exposure chamber and put in contact with the external surface of the glove samples. In case of powder nanoparticles, a second thin circular nitrile membrane is placed on top of the sample to enclose the nanoparticles and prevent them from dispersing in the exposure chamber. The physiological/sampling chamber plays the dual role of allowing the detection of nanoparticles having crossed the sample membrane as well as simulating the microclimate inside gloves. This includes the control of temperature and humidity conditions as well as a contact with physiological solutions at different pH simulating sweat. The whole system is enclosed in a glove box to ensure the operator safety during assembly, dismounting and clean-up operations as well as during the tests.

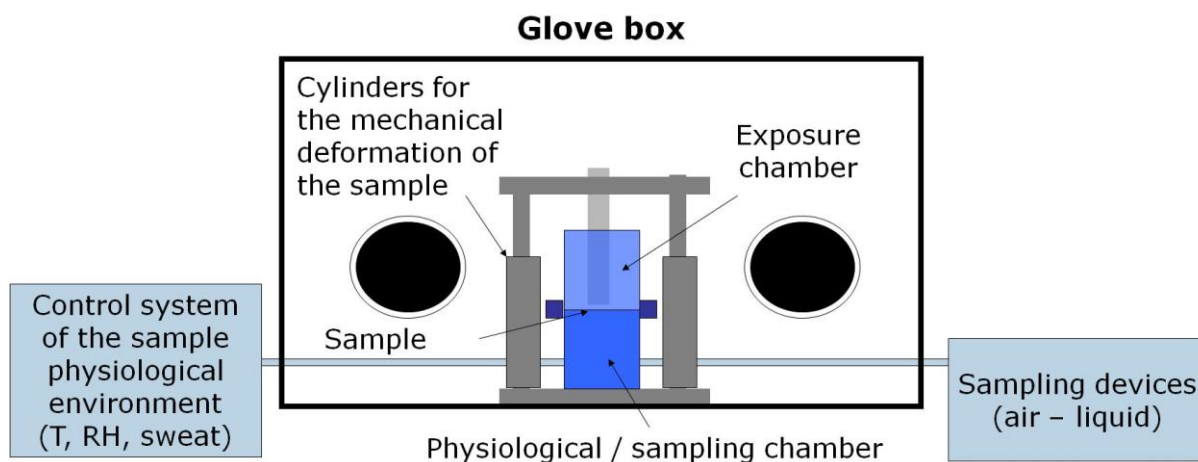


Figure 4. Schematic representation of the test setup.

Mechanical constraints subjected to gloves while in use are simulated by a system of cylinders and probe heads of various shapes and sizes. They are used to deform the sample while it is exposed to nanoparticles. A load cell and a displacement sensor allow a computer control and characterization of these mechanical stimuli. Four probe heads have been fabricated as illustrated in Figure 5. Probe A is a 35mm-diameter full cylinder applying an out-of-plane deformation to the sample while pressing on the nanoparticles. Probe B is a 35mm-diameter hollow cylinder used to deform the sample without applying any constraint on the nanoparticles. Probe C is a 35-mm cone with a spherical tip which is used to simulate biaxial deformations corresponding to hand and finger flexion [25]. Finally, probe D is a 50mm-diameter cylinder used for compression in combination with a sample supporting plate. An overflow is connected to the physiological/sampling chamber to accommodate the sampling chamber volume reduction due to sample deformation. The system is computer-controlled so that sample deformations can be applied in a static or a dynamic mode using these four probe heads.

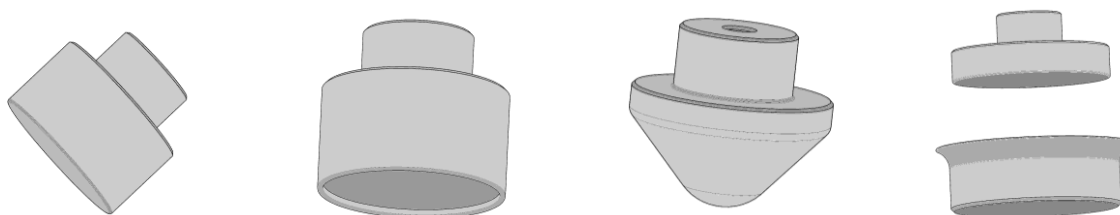


Figure 5. Setup probe heads, a) Probe A, b) Probe B, c) Probe C, and d) Probe D.

3. Investigation of Nanoparticle Detection Techniques

The suitability of a series of nanoparticle detection techniques for the test method has been investigated. This includes the development of specific sampling and sample preparation protocols.

Attempts have been made to use a scanning mobility particle sizer (SMPS, TSI) to detect the presence of nanoparticles in the sampling chamber air. Trials involved two ranges of detection: 2-150 nm and 10-1000 nm, and flow rates of up to 10 L/min. In all cases, nothing but a few isolated nanoparticle detection events were recorded, even when nanoparticles sucked up directly from a container were seen disappearing from it. The reason for the inability to detect nanoparticles using this device was attributed to electrostatic forces strongly affecting nanoparticles [26] and making TiO₂ powder stick to non-conductive surfaces, even to the SMPS graphite silicone tubing (see Figure 6).

A second set of investigated nanoparticle detection techniques involved field emission gun SEM (FEG-SEM), atomic force microscopy (AFM) and TEM for analyzing the inner (sampling chamber side) surface of glove samples. As illustrated in Figure 7 with a FEG-SEM (JEOL JSM-7600F) image of a TiO₂ aggregate on the surface of a nitrile glove, direct observation of nanoparticles on the glove sample surface happens to be highly imprecise due to the similarity between nanoparticles and glove surface features as well as to the difficulty in locating a few nanoparticles over a large sample area. Positioning TEM grids on the inner surface of glove samples (facing the physiological/sampling chamber) was also not an option because of the deformations subjected to membranes during the tests. Future attempts will be made to place charged TEM grids on a support at the bottom of the physiological/sampling chamber.



Figure 6. Picture of the SMPS sampling line inlet covered with TiO₂ powder.

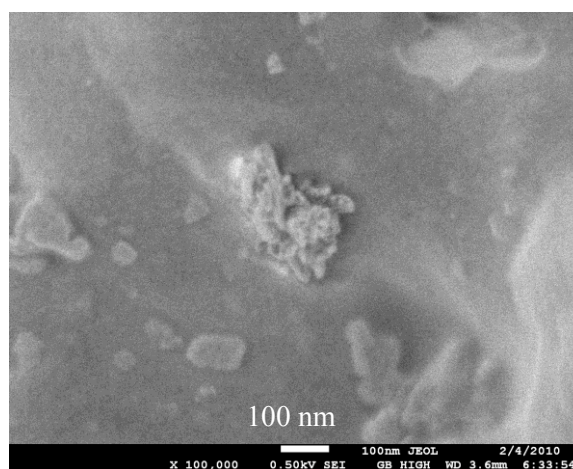


Figure 7. FEG-SEM image of TiO₂ nanoparticles on the surface of a nitrile glove.

In order to allow using microscopy techniques to detect nanoparticles in the physiological/sampling chamber despite the natural tendency of TiO₂ nanoparticles to stick to the chamber walls, a special sampling protocol was developed. It involves adding a 10-mm thick layer of methanol in the

physiological/sampling chamber before closing it with the sample membrane during setup assembly. Heights of membrane deformations are such that no contact between the sampling solution and the sample surface occurs during the tests. When the experiment is over and before dismantling the test setup, the chamber assembly is gently tilted and rotated so that the liquid can rinse the physiological/sampling chamber walls as well as the sample surface. The sampling solution is then collected in a vial and centrifuged on a carbon-coated copper grid or on a mica substrate for further observation by TEM, AFM or FEG-SEM [27].

The last category of investigated nanoparticle detection techniques deals directly with liquids. The first one is inductively coupled plasma mass spectrometry (ICP-MS). The sampling protocol involving a 10-mm thick layer of sampling solution rinsing the physiological/sampling chamber was also applied, but with a 1% nitric acid solution in ultra high purity (UHP) water according to the methodology developed by Kaegi et al. [28]. The second technique is nanoparticle tracking analysis (NTA). In that case, the sampling solution is made of UHP water.

4. Results and Discussion

A first set of experiments was performed to characterize the effect of mechanical deformations and liquid carriers used in TiO₂ colloidal solutions on the glove materials. The swelling behaviour of the four elastomers was assessed by weight and length change measurements on 4x50mm samples immersed in the three TiO₂ colloidal solutions as well as in solvents corresponding to the liquid carriers, i.e. water, ethylene glycol and 1,2-propanediol, over a period of two hours. Samples were cut along the glove transverse and longitudinal directions and at least 3 replicates were measured for each condition. Increases in sample weight and length have been observed in some cases, essentially with latex and nitrile rubber membranes. Figure 8 illustrates for example the variation in nitrile rubber glove transverse length ($(l-l_0)/l_0$, with l and l_0 respectively the length of the exposed and unexposed samples) as a function of immersion time in TiO₂ colloidal solutions in water and 1,2-propanediol. This increase in sample weight and length may indicate a penetration into the elastomer membranes of the solvents used as liquid carrier in the TiO₂ colloidal solutions. If these diffusing solvents act as carrier for TiO₂ nanoparticles through the polymer membranes, they could increase their penetration rate through the gloves. In some instances, a small and gradual weight loss over time was recorded after the initial increase. This may be due to a release of leachable additives from the glove material during the swelling process. In the case of latex and nitrile rubber, a difference in swelling behaviour depending on the sample orientation (transverse or longitudinal) was noted as illustrated in Figure 9 for nitrile rubber immersed in 1,2-propanediol. This phenomenon may be due to the anisotropy in the glove mechanical properties which results from the dipping manufacturing process.

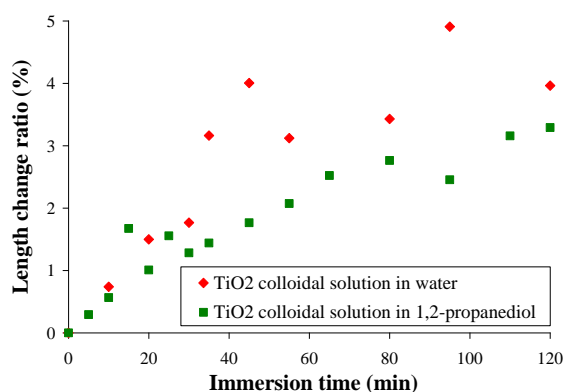


Figure 8. Variation in transverse length vs. immersion time for nitrile rubber in TiO₂ colloidal solutions in water and 1,2-propanediol.

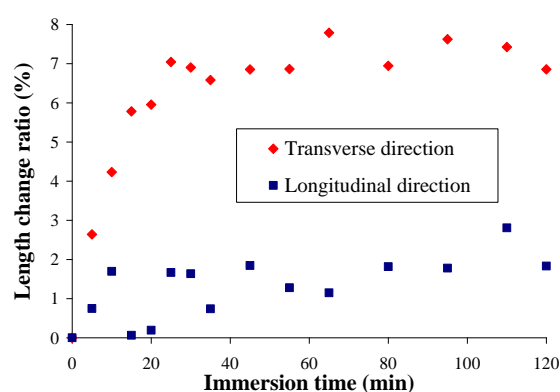


Figure 9. Variation in sample length as a function of immersion time in 1,2-propanediol for transverse and longitudinal nitrile rubber samples.

The effect of mechanical deformation and exposure to TiO₂ colloidal solution liquid carriers on the glove surface morphology was investigated using the test setup described in Section 2. Dynamic biaxial deformations were applied to glove samples for 7 hours using Probe C, a maximum probe displacement of 40 mm (corresponding to a strain of about 80%) and a frequency of 0.0033 Hz (1 deformation every 5 minutes). Sample exposure to ethylene glycol and 1,2-propanediol was performed using the test setup, either by itself also for a period of 7 hours or with simultaneous application of dynamical mechanical deformations to the sample. The surface morphology of both sides of samples exposed to solvents, deformations or combination of both was analyzed by SEM (Hitachi S3600N). The quantification of the induced surface modifications compared to unexposed gloves was performed on the basis of the surface area of surface features specific to each material (described in Section 1.2): pores for nitrile rubber, cracks for neoprene and platelets for latex and butyl rubber. Figure 10 displays the result of this analysis in the case of 1,2-propanediol used as solvent and for the glove sample external surface (on the side of the exposure chamber). Both solvent exposure and deformations appear to strongly affect the external surface of latex gloves and, to a lesser extent, that of butyl rubber ones. The last two materials seem to be only affected by mechanical deformations, with a larger effect produced in the case of nitrile rubber. A similar behavior was observed with ethylene glycol. The effect of mechanical deformations observed on the glove external surface might include an abrasion contribution induced by the probe rubbing on the sample surface. This hypothesis is supported by the reduction in surface features observed when the mechanical deformations are combined with exposure to glycols playing the role of a lubricating agent. Analysis of the other side of the samples, i.e. on the glove inner surface facing the physiologic/sampling chamber, only revealed significant modifications in surface features for latex, with the same trend as for the external surface. These results show that deformations and exposure to TiO₂ colloidal solution liquid carriers may induce damages in glove materials which could facilitate the penetration of nanoparticles through the membrane.

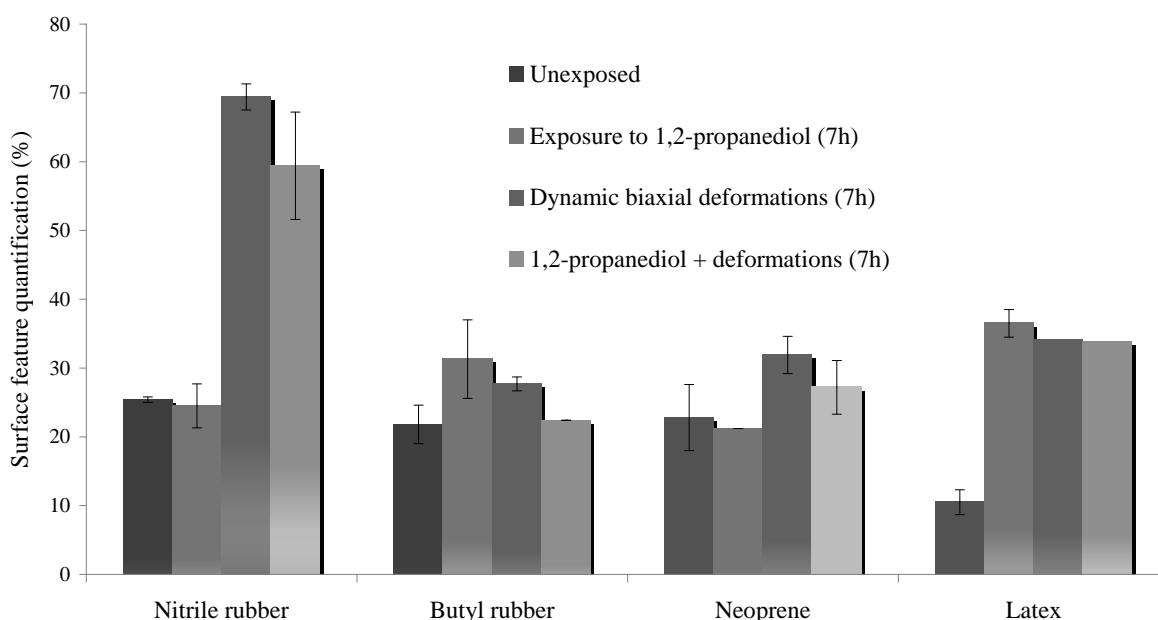


Figure 10. Effect of 7h exposure to solvent, dynamic biaxial deformations and solvent + deformations on material-specific glove surface features for nitrile rubber, butyl rubber, neoprene and latex samples.

Measurement of nanoparticle penetration through the four glove materials has been performed using the developed test setup (see Figure 4) and TiO₂ powder. Glove samples were subjected to dynamical biaxial deformations (Probe C, 1 deformation every 5 minutes, 40mm maximum probe displacement) while being exposed to TiO₂ powder (250 mg deposited on the sample in the exposure chamber) for periods of 1 hour 30 minutes, 3h, 5h and 7h. A 10-mm layer of sampling solution (1% nitric acid solution in UHP water) was present in the sampling chamber during the experiment and used to rinse the sampling chamber walls when the test was over. The collected sampling solutions were then analysed by ICP-MS. The results obtained with nitrile and butyl rubber samples are displayed in Figure 11. A gradual and clear increase in Titanium concentration in the sampling solutions is observed, which may indicate a penetration of TiO₂ powder through the glove samples as a result of mechanical deformation. In addition, an observation by FEG-SEM of the exposed side of the sample surfaces after excess TiO₂ has been removed seems to point towards a reduction in the size of nanoparticle agglomerates as test time increases. Even if these results are very preliminary and need to be replicated, they indicate a possible penetration of TiO₂ nanoparticles through protective gloves when subjected to mechanical deformations over a period of time. They also demonstrate that ICP-MS in combination with the 1% nitric acid / UHP water sampling solution protocol is an appropriate detection technique for the nanoparticle penetration test method.

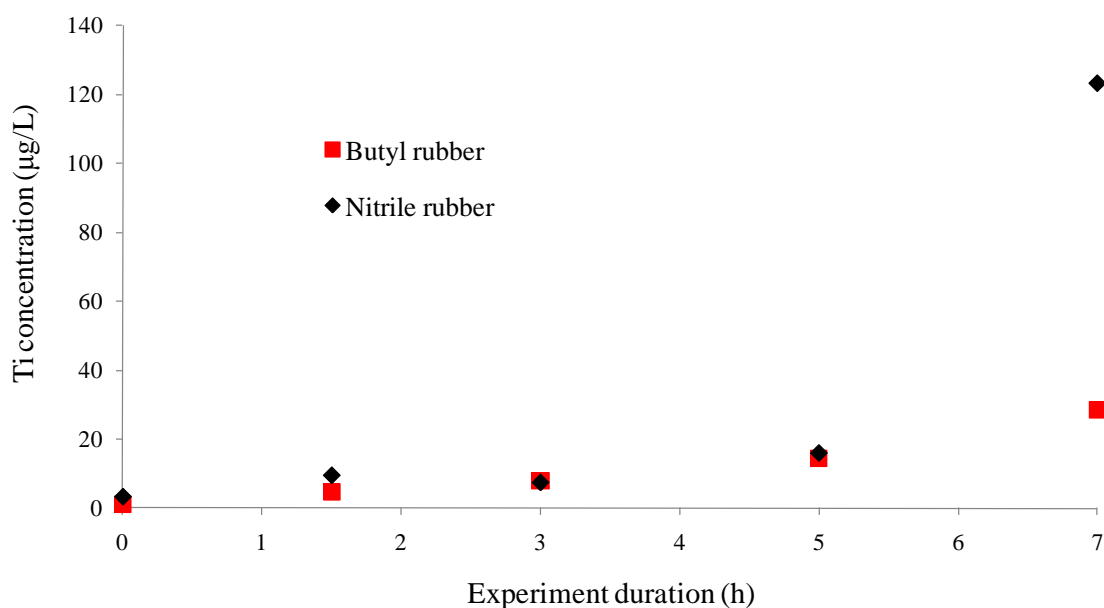


Figure 11. Variation in Ti concentration in the sampling solutions as a function of test time for nitrile and butyl rubber samples exposed simultaneously to biaxial deformations and TiO₂ powder.

5. Conclusions

A test method has been developed to measure the penetration of nanoparticles through protective gloves in conditions simulating occupational use. It involves nanoparticles applied as powder and colloidal solutions. In addition, samples can be subjected to various types of static and dynamic mechanical deformations simultaneously with nanoparticle exposure. Finally, the presence of a microclimate inside the glove is simulated by the use of a physiological solution in contact with the sample as well as a control of temperature and humidity conditions.

The development of the test method also involves the identification of appropriate nanoparticle detection techniques. A sampling protocol based on the use of a sampling solution rinsing the sampling chamber has been designed for collecting nanoparticles having crossed glove samples.

Methanol-based sampling solutions are centrifuged on grids or mica substrates for analysis by microscopy techniques. On the other hand, NTA and ICP-MS may also be used to directly detect nanoparticles in water-based sampling solutions.

Results have been obtained with commercial 15nm TiO₂ nanoparticles - powder and colloidal solutions in 1,2-propanediol, ethylene glycol and water - and four protective glove materials: nitrile rubber, latex, neoprene and butyl rubber. They show that glove materials are affected by exposure to TiO₂ colloidal solution liquid carriers and mechanical deformations. In addition, preliminary data obtained with the developed test setup and TiO₂ powder seem to indicate a possible penetration of nanoparticles through protective gloves when subjected to mechanical deformations over a period of time. These results demonstrate the need for research in this area.

Acknowledgments

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