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Which Gloves Are Efficient To Protect Against Titanium Dioxide Nanoparticles In Work Conditions?

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Abstract **-** Recent articles underline the potential health risks associated to the "nano" revolution. Titanium dioxide nanoparticles ($nTiO_2$) are one of these engineered nanoparticles (ENP) that have been cautioned about their likely harmful effects on health. In occupational use, to handle ENP, many Health & Safety agencies have recommended the application of the precautionary principle namely the recommendation of the use of protective gloves against chemicals. However, at the best of our knowledge, no study about the penetration of ENP through protective gloves in working conditions was performed.

This study was designed to evaluate the efficiency of several models of protective gloves against $nTiO_2$. Two types of nitrile rubber gloves (100 µm and 200µm), latex and butyl rubber gloves were brought into contact with $nTiO_2$ in water, in propylene glycol (PG) or in powder. Mechanical biaxial deformations (BD), simulating the flexing of the hand, were applied to the samples during their exposure to ENP.

Depending the model of gloves and the mode of application of the NP, the results obtained by ICP-MS (Inductively Coupled Plasma – Mass Spectrometry) are different. For $nTiO_2$ in water, the passage is highlighted for nitrile rubber gloves (100 µm) after only 60 deformations and the $nTiO_2$ concentration reaches its maximum for 180 DB. Regarding the $nTiO_2$ in powder, nitrile rubber gloves (100 µm) and butyl rubber, the values achieved are significant but less than the solutions.

Keywords**:** TiO_2 nanoparticles, Protective gloves, Work conditions, Glove efficiency, ICP-MS.

1. Introduction

The increasing use of ENP in commercial products and industrial processes make their occupational exposures inevitable (Bello et al. 2012). Indeed, the global market for nanotechnologies will attain over 2.5 trillion dollars in 2020 (Maynard 2005) and at the same time, the workers and the researchers in this industry will reach 6 million persons (Roco et al. 2010). Concerning $nTiO_2$, they are increasingly present in several commercial products like paints, varnishes, sunscreens, etc. (Robichaud et al. 2009). But recently, the International Agency for Research on Cancer (IARC) has classified nanosized titanium dioxide in 2B-group as possibly carcinogenic to humans (IARC 2010). This decision follows numerous studies caution about their likely harmful effects on health. For example, a small increase in the number of cancer among workers in contact with $nTiO_2$ has been reported (Web-1). Moreover, studies conducted on rats and mice, which were exposed to 250 nm TiO_2 pigment and 20 nm $nTiO_2$ instilled by intratracheal, recorded the occurrence of pulmonary effects. The observed inflammatory response was higher with $nTiO_2$ (Höhr et al. 2002; Warheit et al. 2006; Warheit et al. 2007, Sun et al. 2012).

In response to IARC's classification, several Health & Safety government agencies have recommended the application of the precautionary principle (Ostiguy et al. 2009; OECD 2010) like the use of protective gloves against chemicals even if no thorough scientific validation of their efficiency against nanoparticles has been made yet.

At the best of our knowledge, three groups have reported research carried out on protective gloves against nanoparticles but most of it involves aerosols. In 2008, Golanski et al has reported the diffusion of

30 and 80 nm graphite nanoparticles through nitrile, vinyl, latex and neoprene commercial glove samples (Golanski et al. 2008) then a year later, the same group measured no penetration for the same gloves with 40 nm graphite and 10 nm TiO_2 and Pt particles (Golanski et al. 2009). In 2010, Park et al. studied the penetration of silver nanoaerosols (AgNP) through nitrile rubber and latex gloves using the same experimental setup than Golanski (Park et al., 2011). The authors have concluded to a non-penetration of AgNP through latex and nitrile rubber protective gloves. All these results seem conflicting.

Exposure to nanoparticles in occupational settings may also involve solutions. This situation is especially relevant to protective gloves. Vinches et al. exposed nitrile glove samples to $nTiO_2$ solution in water with dynamic deformations simulating flexing (Vinches et al. 2013). ICP-MS analyses of sampling solutions suggest the penetration of the nitrile gloves when they were subjected to dynamic mechanical deformations for periods of 5 hours or more.

This paper evaluates the efficiency of four common models of protective gloves against $nTiO_2$ in solutions or in powder in conditions simulating occupational use.

2. Materials

2. 1. Protective Gloves

Four models of protective gloves corresponding to three types of elastomers were selected for this study: disposable latex gloves (100 µm thick), disposable nitrile rubber gloves (100 and 200 µm thick) respectively identified as NBR-100 and NBR-200, and butyl rubber gloves were also used (350 µm thick). All the samples were taken from back and the palm section of the gloves.

2. 2. Nanoparticles

$nTiO_2$ was been selected for this work due to its use in various industrial applications (paints, cosmetics, electronic compounds, etc.) (Robichaud et al. 2009). $nTiO_2$ is labelled as 99.7% pure anatase with an average particle size of 15 nm. Two types of $nTiO_2$ solutions were employed: in water (15 wt%, Nanostructured & Amorphous Materials, Inc., Houston, TX) and in 1,2-propanediol, PG (20 wt%, MK Impex, Mississauga, ON). $nTiO_2$ in powder were also used (Nanostructured & Amorphous Materials, Inc., Houston, TX).

3. Methods

3. 1. Characterization of the $nTiO_2$

A series of experiments were performed to characterize the nanoparticles solution. Firstly, analysis of the $nTiO_2$ stock solution (following dilution to 10 mg L^{-1}) by fluorescence correlation spectroscopy (FCS) gave a hydrodynamic diameter (Domingos et al. 2009). Secondly, thermogravimetric analysis (TGA, Diamond TGA/DTA Perkin Elmer) was used to evaluate the mass ratio of the $nTiO_2$ and to identify the presence of chemicals in the colloidal solutions, in addition to the liquid carrier. Gradual evaporation of the liquid carrier occurred between 25 and 150 ºC with a step of 5°C/min (Vinches et al. 2012). Finally, similar comparisons were performed for the technical grade and ultra-high purity solvents and the $nTiO_2$ suspensions using Fourier transform infrared spectroscopy (FT-IR, Nicolet Continuum XL). Measurements were made in attenuated total reflectance (ATR) mode, between 500 and 4000 cm^{-1}, on drops of solutions after almost total evaporation of the solvent (Vinches et al. 2012). To obtain statistically significant data, triplicate measurements were performed for all tests.

3. 2. Characterization of the Protective Gloves

The surface morphology of five samples for each elastomer was analysed by scanning electron microscopy (SEM, Hitachi S3600N – Vacc = 15 kV – magnification × 1000) (Vinches et al. 2013). A gold layer is deposited by metallization on the samples. The conductive layer obtained with a vacuum metallizer has a controlled uniform thickness (15 nm) over the entire sample's surface. Some characteristic features can be observed on the gloves surface: micrometer-size pores for nitrile rubber, cracks for latex and platelets for butyl rubber gloves. The quantification of the surface area of these features was performed using the software ImageJ (image processing).

In the same time, a XPS (X-ray photoelectron spectrometry) modulus is employed to perform chemical analyses of the glove materials, particularly to evaluate the presence or absence of titanium dioxide, used as reinforcing fillers (Mellstrom and Bowan 2005).

3. 3. Mechanical Deformations Experimental Setup

For the purpose of this study, a test setup has been developed and is illustrated in Fig. 1. It includes an exposure chamber and a sampling chamber, which are separated by the sample. Both chambers and all elements in contact with NP are made of ultrahigh molecular weight polyethylene to limit the effect of adsorption of $nTiO_2$ in solution. The setup has been designed to allow exposing glove samples to both NP when simultaneously subjecting them to dynamic mechanical constraints. $nTiO_2$ are introduced (6 mL $nTiO_2$ solution and 250 mg for $nTiO_2$ in powder) in the exposure chamber and put in contact with the external surface of the glove samples. As shown in Fig. 1, the test setup is also equipped with a probe linked to an electronic system for controlling mechanical deformations to the sample. The system is computer controlled and includes a 200-N load cell and a position detector. 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.

The time profile of sample deformations corresponding to the results reported in this paper is a 50% deformation every minute. The maximum of BD is fixed to 180 for NBR-100, NBR-200 and latex gloves. In fact, this value corresponds approximately to 3-hours wearing time. Normally, after this time these gloves models should be discarded. Concerning butyl rubber gloves (non-disposable gloves) the maximum of BD is fixed to 420 (7-hours wearing time).

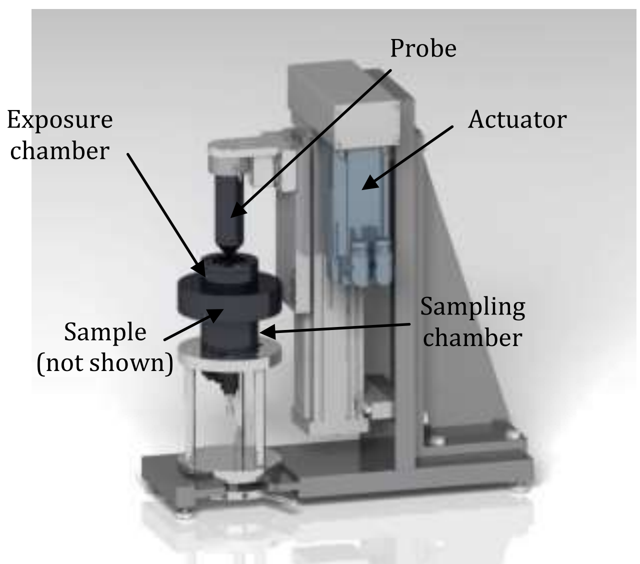

Fig. 1 Isometric view of the test setup.

3. 4. ICP-MS Analysis

The preparation of the sampling solutions for ICP-MS (PerkinElmer NexION 300X) analyzes was performed following a protocol established by Shaw et al. (Shaw et al. 2013). Firstly, to minimize adsorption phenomena, aggregation and agglomeration, all sample solutions were stirred vigorously and placed in an ultrasonic bath (Branson model 5510) for 20 minutes. Secondly, 4 mL of sampling solution is acidified to 2% with the addition of 150 µL of pure nitric acid (Fluka Analytical , $HNO_3 \geq 65\%$, the presence of Ti $\leq$ 0.01 mg / kg). Finally, 1 mL of a 10%-Triton X-100 is added. Triton X- 100 is a non-ionic surfactant in liquid form. According to Shaw, Triton X-100 facilitates the $nTiO_2$ dispersion in the matrix. Before being analyzed by ICP- MS, each sample was stirred during 10 seconds.

ICP-MS does not measure directly $nTiO_2$ concentration ($[nTiO_2]$) but the concentration of Ti^{4+} ($[Ti^{4+}]$). Indeed, after the introduction of the sampling solution, $nTiO_2$ are ionized according to Equation (1) that is corresponding in molar concentration terms at the Equation (2).

$$nTiO_2 \rightarrow Ti^{4+} + 2O^{2-} \tag{1}$$

$$[TiO_2] = [Ti^{4+}] = 2[O^{2-}] \tag{2}$$

ICP-MS give mass concentration expressed in µg/L. To convert molar concentration to mass concentration, we must multiply the molar concentration by the molar mass of chemical compound as Equation (3):

$$[TiO_2] \times M_{TiO_2} = [Ti^{4+}] \times M_{Ti^{4+}} \tag{3}$$

With $M_{TiO_2} = 79.866\ g/mol$ and $M_{Ti} = 47.867\ g/mol$. So, a proportional relationship can be established between the mass concentrations of $nTiO_2$ and Ti^{4+} (Equation (4)):

$$[TiO_2] = 1.668 \times [Ti^{4+}] \tag{4}$$

In addition, titanium has five naturally occurring isotopes. ICP-MS measure simultaneously the concentrations of four of them: ^{46}Ti, ^{47}Ti, ^{48}Ti, ^{49}Ti. To minimize interference with other chemical groups, for example $S - H$ group, only the concentrations of ^{47}Ti are retained.

4. Result and Discussion

4. 1. Characterization of the $nTiO_2$ Solutions

FCS analyses were performed to measure the hydrodynamic diameter of the $nTiO_2$ solutions. 21 ± 2 nm were obtained for $nTiO_2$ in water. The same analysis was not possible for the $nTiO_2$ in PG due to an incompatibility between the cell material and the colloidal solution liquid carrier. Thermogravimetric analyses were also carried out to estimate the $nTiO_2$ mass fractions. The mass fraction obtained for $nTiO_2$ in water is 14.3 ± 0.8 % and 25.0 ± 3.7 % for $nTiO_2$ in PG. These results confirmed the manufacturer data. In addition, FT-IR analyses were performed to bring out the presence of additives such as stabilizing agents. An additional peak appears at 1070 cm^{-1} for the $nTiO_2$ in water (no shown) compared to the spectrum of milli-Q water. This peak may be associated with the elongation of a CO bond. It might indicate the presence of an alcohol or ether used as additive in the $nTiO_2$ solution. On the other hand, the spectra of $nTiO_2$ in PG and the ultra pure PG do not disclose any significant difference. In these cases, spectra exhibit a complex structure which explains the difficulty in detecting additional peaks associated with the presence of additives.

4. 2. Characterization of the $nTiO_2$ Powder

The size distribution of the $nTiO_2$ was measured by transmission electron microscopy (TEM, JEM-2100F) and verified by statistical analysis of 174 particles. Two allotropic forms of TiO_2 were observed: a spherical anatase and a rod-like rutile (Fig. 2(a)). Analysis by X-ray diffraction (Philips X'PERT) confirmed the presence of 3 to 6% rutile in the $nTiO_2$. Fig. 2(b) displays the size distribution of the analysed sample in terms of circular diameter. It can be seen that the average dimension of the particles/aggregates was situated around 100 nm, although even some micrometric-size agglomerates were recorded. In fact, only two particles with a diameter lower than 20 nm were counted.

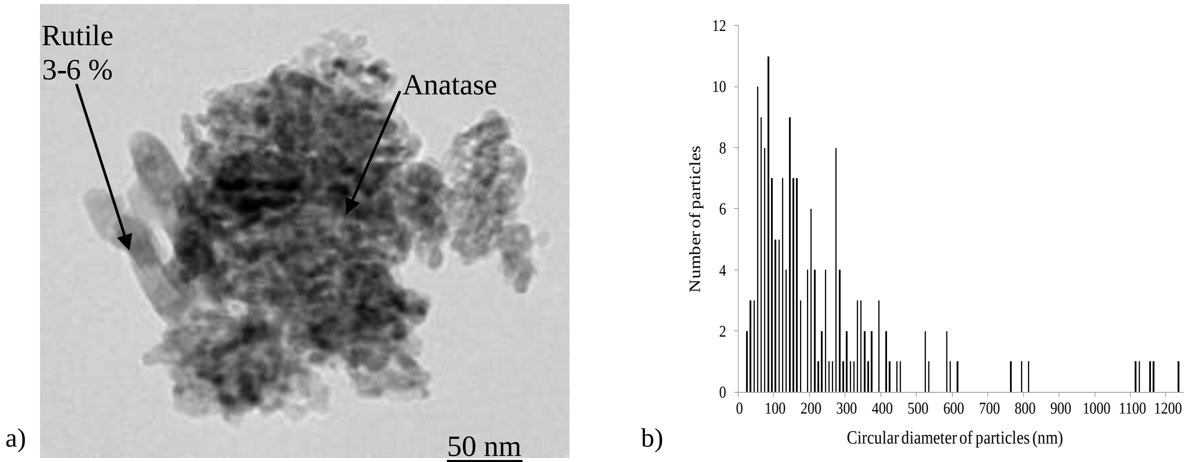

Fig. 2(a) TEM image of the $nTiO_2$ powder and Fig.2(b) Size distribution of the $nTiO_2$ powder.

4. 3. Characterization of the Protective Gloves Surface

Micrometer-size surface features which can be observed on the outer surface (surface in contact with the $nTiO_2$) of all the protective gloves (Fig. 3). For both nitrile rubber gloves, the surface features corresponding to pores, cracks for latex glove and platelets for butyl rubber gloves. These surface features may facilitate the penetration of $nTiO_2$ through protective gloves.

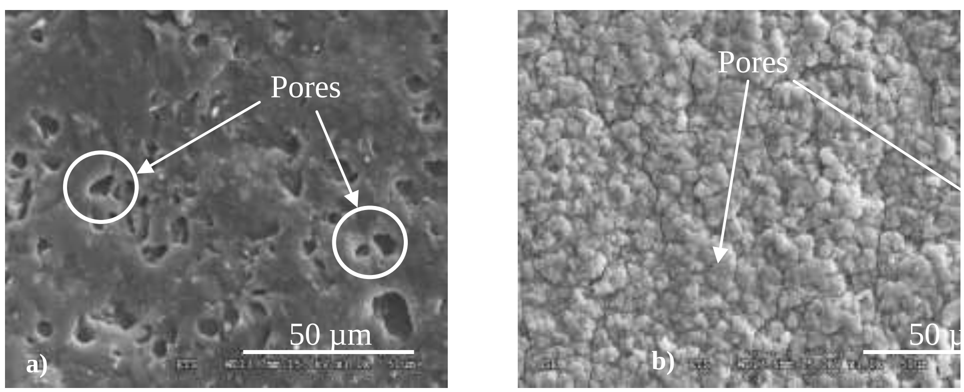

Fig. 3 SEM images of the native outer surfaces of protective gloves (a) NBR-100 and (b) latex.

XPS chemical analyses of the glove material have been made. Triplicate measurements were performed for all analyses. The mass concentrations of titanium measured are (0.44 ± 0.08) for NBR-100 and (0.73 ± 0.14). No trace of titanium is detected for latex and butyl rubber gloves. To ensure that the titanium concentration in the sampling chamber is due to the passage of $nTiO_2$ and not to the glove degradation, some tests were performed without NP.

4. 4. ICP-MS Results

The variation of Ti^{4+} concentration in the sampling solutions as a function of the number of deformations is reported in Fig. 4 and corresponding to NBR-100 samples in contact or not with $nTiO_2$ solutions. To obtain statistically significant data, triplicate measurements were performed for all analyses. Initial tests were performed without $nTiO_2$ to determine the possible contamination by titanium content in nitrile rubber gloves. The average value of Ti^{4+} concentration is 0.4 µg/L (dashed line in Fig. 4). Similarly, in the presence of $nTiO_2$ in PG, no penetration of NP is remarkable. This result indicates that NBR-100 is efficient against the penetration $nTiO_2$ in PG under work conditions. By cons, for $nTiO_2$ in water, the maximum value of Ti^{4+} concentration is reached for 180 DB (2590 µg/L). According to the Equation (4), $nTiO_2$ concentration is 4320 µg/L. It may be noted that $nTiO_2$ concentration is 12.8 µg/L after 60 BD and 271.9 µg/L after 120 BD. This result can be explained by a progressive deterioration of these protective gloves. No significant Ti^{4+} concentration was measured for NBR-200, latex and butyl gloves in contact with $nTiO_2$ in solutions.

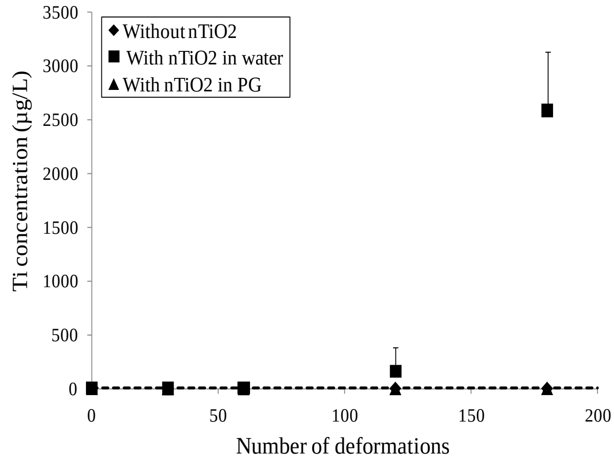

Fig. 4. Titanium concentration in the sampling solutions as a function of the number of deformations for NBR-100 samples exposed to $nTiO_2$ solutions.

Same tests were performed with $nTiO_2$ in powder. In this case, no major Ti^{4+} concentration was measured for NBR-200 and latex gloves. By cons, for butyl rubber, Ti^{4+} concentration reached 10.9 µg/L after 420 BD (Fig. 5). Similarly, a significant increase in Ti^{4+} concentration was detected with NBR-100. However, these results should be confirmed because the protocol established by Shaw et al. (Shaw et al. 2013) gives a yield of 45% with $nTiO_2$ in powder whereas it reaches 85% with $nTiO_2$ in solutions.

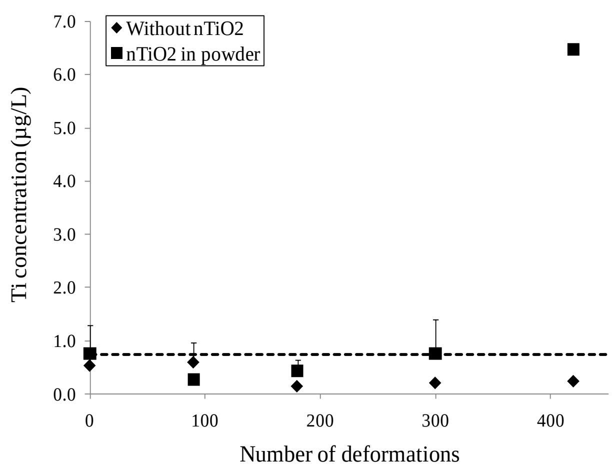

Fig. 5. Variation in titanium concentration in the sampling solutions as a function of the number of deformations for butyl rubber samples exposed to $nTiO_2$ in powder.

4. Conclusion

This work has experimentally evaluated the efficiency of protective gloves against the $nTiO_2$ under work conditions. The results are different depending on the glove models and the $nTiO_2$ application mode. Table 1 summarizes the efficiency of all the protective gloves studied against $nTiO_2$.

Table 1. Efficiency of protective gloves.

	NBR-100	*NBR-200*	*Latex*	*Butyl rubber*
$nTiO_2$ in water	**Poor**	Good	Good	Good
$nTiO_2$ in PG	Good	Good	Good	Good
$nTiO_2$ in powder	**Weak**	Good	Good	**Poor**

In the case of NBR-200, the thickness has a major role as barrier whereas for latex gloves, the chemical composition seems to be the main actor in the efficiency. Some tests are needed to confirm the results obtained with $nTiO_2$ in powder. So we need for further investigations but for the moment, great care must be taken in selecting protective gloves for the handling $nTiO_2$. It is already possible to recommend a frequent replacement of gloves in case of exposure to $nTiO_2$.

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