Experimental evaluation of the resistance of nitrile rubber protective gloves against TiO$_2$ nanoparticles in water under conditions simulating occupational use

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Abstract – Manufactured nanoparticles (NPs), including titanium dioxide nanoparticles (nTiO$_2$), now enter in the formulation of several commercial products. Some studies have been carried out to assess the resistance of protective gloves against NPs, they have generally not considered the conditions prevailing in occupational settings. This study was designed to evaluate the behavior of protective gloves materials against NPs in solution under conditions simulating occupational use. Mechanical deformations, simulating those produced by flexing the hand, were applied to nitrile rubber glove samples in contact with nTiO$_2$ in water. The first analysis showed that nTiO$_2$ solution penetrates some of the materials after prolonged dynamic deformations. These results were partly attributed to modifications in the physical and mechanical properties of protective gloves materials that were induced by repetitive mechanical deformations and/or the presence of the colloidal solution.

1. Introduction

The global market for nanotechnologies should represent more 2.5 trillion dollars in 2015 [1] and the National Science Foundation has estimated that the number of nano-products manufactured around the world will double every three years until 2020. At the same time, the number of workers and researchers in the industry will reach 6 million [2]. Titanium dioxide nanoparticles (nTiO$_2$) are present in commercial products such as paints, varnishes, sunscreens, etc. [3, 4] and represent a new potential source of hazard. Indeed, some concerns exist about their potential noxious effects on health. For example, studies conducted on rats and mice, exposed to 250-nm TiO$_2$ pigment particles and 20-nm nTiO$_2$, observed a greater occurrence of pulmonary effects [5]. In addition, the observed inflammatory response was higher with nTiO$_2$ [6, 7]. In 2007, a small increase in the number of cancers among workers in contact with nTiO$_2$ has been reported [8]. Based on these results, the International Agency for Research on Cancer (IARC) has classified nanosized titanium dioxide in the 2B-group, as being possibly carcinogenic to humans [9]. Furthermore, some studies have shown that the skin is not an impervious membrane against NPs. The penetration, through epidermal layers, is possible when the skin presents small lesions [10], after repeated flexion [11] or even intact [12]. In response to these studies and the IARC classification, several agencies have recommended application of the precautionary principle (e.g.[13]). While this implies the use of protective gloves, the number of studies on dermal protection against NPs, and especially on gloves, is scarce.
Whereas the penetration of 30 and 80 nm graphite NPs has been reported for nitrile, vinyl, latex and neoprene commercial glove samples [14], no penetration was observed for the same glove models for 40 nm graphite, 10 nm TiO\textsubscript{2} or Pt nanoparticles [15, 16]. For his part, Ahn et al. exposed nitrile and latex glove samples to nanoclays and alumina nanopowder [17]. Scanning electron microscope (SEM) observations revealed the accumulation of the NPs in micrometer-size pores at the surface of the gloves material.

In occupational settings, protective gloves are subjected to mechanical deformations, for example biaxial strains at interphalangeal joints which may also affect the penetration of NPs [18]. Moreover, the presence of a liquid carrier facilitates the penetration of NPs because elastomers are sensitive to solvents and induce a significant swelling [18, 19]. This paper reports some results on the penetration of nTiO\textsubscript{2} in water through protective gloves. The tested protective glove materials consisted of nitrile rubber. It also analyses the effect of contact of the glove materials with the colloidal solution liquid carrier as well as of dynamic biaxial deformations.

2. Materials

2.1. Protective gloves
Two models of protective gloves were selected for this study: disposable nitrile rubber gloves with 100 and 200 µm thickness. In this paper, the corresponding results are identified, respectively, as NBR-100, NBR-200. All the samples were taken from the palm section of the gloves.

2.2. Nanoparticles
Nanoparticle suspension in water used for this study contained 15 nm, anatase titanium dioxide nanoparticles (15% w/w). It was obtained from Nanostructured & Amorphous Materials, Inc. (Houston, TX). Particle sizes of 21 ± 2 nm were measured by fluorescence correlation spectrometry (FCS) [20].

3. Methods

3.1. NP penetration experimental setup
An experimental test setup has been developed for the purpose of this study (Figure 1). It has been designed to expose glove samples to colloidal solution while simultaneously subjecting them to biaxial constraints simulating deformations produced by flexing the hand. The test system includes two chambers, an exposure chamber and a sampling chamber, as well as all components are made of ultrahigh molecular weight polyethylene loaded with black carbon in order to limit the adsorption of nTiO\textsubscript{2}. Both chambers are separated by the sample. Colloidal solution is introduced in the exposure chamber and placed into contact with the external surface of the glove sample. As shown in Figure 1, the test setup is also equipped with a probe mounted on an electrical system for deforming the sample. The system includes a 200 N load cell and is computer controlled. The whole setup is enclosed in a glove box in order to ensure operator safety during assembly, dismounting and clean-up operations, as well as during tests.
As illustrated in Figure 2(a), the time profile of the sample deformations consists in 50% out-of-plane deformations applied every 1 or 5 minutes. The probe head used in this study is shown in Figure 2(b) and corresponds to a conical-spherical geometry which simulate biaxial deformations (BD) produced by flexing hand [21].

3. NP sampling protocol and detection methods

nTiO$_2$ sample collection was facilitated using a sampling solution (ultra-high purity water with 1% nitric acid) which was placed in the sampling chamber during setup. Before the beginning of each test, the absence of contamination of the sampling chamber by nTiO$_2$ was verified by analysing a control sample that was produced by rinsing the sampling chamber with the sampling solution. If a trace of contamination in the test control was detected, the result of the following test was discarded. Titanium concentrations were analysed by ICP-MS (Inductively coupled plasma mass spectrometry, Varian 820).

3. 3. Chemical composition of the glove surface and quantification of the characteristic features.
Energy dispersive spectroscopy (EDS) analysis was conducted with Oxford INCA X-sight 200 to perform the quantitative analysis of the chemical elements present in both glove materials. Moreover, some characteristic features (micrometer-size pores) can be observed on the glove surface as already reported in the literature [17]. The surface morphology of five samples for each elastomer, was analysed by scanning electron microscopy (SEM, Hitachi S3600N – Vacc = 15 kV – magnification × 1000). The quantification of the surface area of these features was performed using image processing software.

3. 4. Strain energy
In order to follow the variation of the strain energy corresponding to the applied 50% dynamic deformation during tests, stress-strain curves were plotted. An estimation of the relative strain energy was carried out by computing the area under the curves using the trapezoidal method.

3. 5. Swelling measurements
Length change measurements were performed on glove samples in order to evaluate the effect of the nTiO$_2$ solution. Indeed, elastomers may be sensitive to swelling in some solvents. Rectangular samples (5 × 60 mm) were taken from the palm section of the gloves. To obtain statistically significant data, triplicate measurements were carried out for each solution. The samples were immersed in the nTiO$_2$ in water. At regular intervals, samples were removed from the liquid and their length measured using a calliper (±0.01 mm). The length change data were computed using Eq. (1):

$$\Delta L(t) = \frac{L_t - L_0}{L_0}$$  \hspace{1cm} (1)

with $L_t$ being the length at $t$ time and $L_0$ the corresponding value before immersion.

4. Results and discussion

4. 1. Characterization of the nTiO$_2$ in water and the protective gloves surface.
A series of experiments were performed to characterize the nanoparticle solution. Analysis of the aqueous nTiO$_2$ stock solution (following dilution to 10 mg L$^{-1}$) by fluorescence correlation spectroscopy (FCS) gave a hydrodynamic diameter for the particles of 21 ± 2 nm. Thermogravimetric analyses were carried out to estimate the nTiO$_2$ mass fractions. The mass fraction obtained for nTiO$_2$ in water is 14.3 ± 0.8%. These results confirmed the manufacturer data. In addition, FT-IR analyses were performed to bring out the presence of additives such as stabilizing agents. Figure 3 compares FT-IR spectra of nTiO$_2$ in water and ultra-high purity water. An additional peak can be observed for nTiO$_2$ in water. It may be due to the presence of stabilizing agents.
Figure 3. FT-IR spectra of nTiO2 in water (purple) and in ultra-high purity water (red).

Figure 4 shows the micrometer-size pores which can be observed on the outer surface of both nitrile rubber gloves. The same features were observed on the inner surface. Table 1 compares the mass fraction of the chemical elements for both nitrile rubber gloves. Significant differences exist between the two models of protective gloves but both contain titanium.

| Chemical elements | NBR-100 Mass fraction (%) | NBR-200 Mass fraction (%) |
|-------------------|--------------------------|---------------------------|
| C                 | 85.64                    | 90.27                     |
| O                 | 10.41                    | 5.44                      |
| S                 | 1.24                     | 1.20                      |
| Ca                | 1.85                     | 0.71                      |
| Si                | 0.20                     | 0.38                      |
| Al                | -                        | 0.35                      |
| Ti                | 0.44                     | 0.73                      |
| Zn                | -                        | 1.13                      |

Figure 4. SEM images of the native outer surfaces both nitrile rubber gloves and Table 1 Chemical composition of glove materials obtained by EDS analysis.

4.2. NP penetration: ICP-MS analyses.

Glove samples (NBR-100) were exposed to the nTiO2 in water while being simultaneously subjected to a 50% biaxial deformation every 5 minutes for up to 7 h. In order to determine if the titanium concentration is solely due to the penetration of the nTiO2 solution, the same tests were repeated without NPs. The results are shown in Figure 5. For nitrile gloves, a clear increase in titanium concentration in the sampling solutions can be observed after 5 and 7 h of deformations as a result of the presence of the nTiO2 in the sampling chamber. These results indicate the possible penetration of nTiO2 in water through nitrile gloves after deformations.
These first results have been obtained with conditions simulating soft occupational use (a deformation every 5 minutes up to 7h, for a total of 85 deformations). In typical occupation use, the number of flexions of the hand per minute is probably more important and the wearing time of protective glove does not exceed 3 hours.

Figure 4. Variation in titanium concentration in the sampling solutions as a function of test duration for NBR-100 samples exposed simultaneously to 50% biaxial deformations and nTiO$_2$ in water.

4.3 Mechanical and physical phenomena facilitating the penetration of nTiO$_2$ solution.

In order to investigate the cause of the NP penetration through the nitrile gloves, the swelling of nitrile rubber immersed in nTiO$_2$ solution has been studied. In addition, some mechanical tests were performed to study the behaviour of the gloves material.

Swelling measurements were performed by recording the length change of both nitrile rubber samples after immersion in aqueous nTiO$_2$. Figure 6 displays a gradual length change increase for the two glove materials, indicating significant penetration of nTiO$_2$ solution. Nonetheless, a larger swelling ratio was recorded for NBR-100. For example, for an immersion time of 3 hours, the length change ratio for the NBR-100 was 5% and 2% for NBR-200. It should be noted that maximum was not attained for either of the two nitrile rubber gloves after 3 hours of immersion. A comparison of the length change behaviour was therefore performed over a longer period. A 9% gain in length was observed for the NBR-100 after 20 hours of immersion and a 12% after 8 days of immersion for NBR-200. This difference in behaviour between the two nitrile rubber gloves can be attributed to their difference in chemical composition which induces a different affinity to the colloidal solution. The difference in swelling behaviour between both kinds of protective gloves may well be one of the primary reasons that the aqueous nTiO$_2$ was able to more easily penetrate the NBR.
Figure 6. Variation in length change ratio as a function of immersion time in aqueous nTiO$_2$ for both nitrile rubber samples.

On the other hand, the sample glove surface morphology was characterized following exposure to the dynamic biaxial deformations (BD) without nTiO$_2$ in water. Figure 7(a) displays the variation of the surface features as a function of the number of deformations for NBR-100. In the case of the inner surface, no significant effect is recorded. By cons, the outer surface seems to be strongly affected by mechanical deformations. Indeed, an increase in pore surface area is observed after only 30 BD and more than three-fold after 180 BD. The deterioration of the materials could be attributed to abrasion of the sample surface by the probe [22]. This hypothesis is supported by the reduction in surface features observed when the mechanical deformations are combined with exposure to nTiO$_2$ in water which plays the role of a lubricating agent as shown in Figure 7(b). Such an observation could explain the jump in the Ti concentration in the sampling solution that was measured for NBR-100 after this number of deformations.
A second mechanical test was to measure the relative strain energy during each deformation. As shown in Figure 8, an important decrease of the relative strain energy was observed especially during the first deformations and reached a tray. This phenomenon must be due to the Mullins effect. Indeed, some polymers chains have reached their limit of extensibility and break during the first deformations, reducing the energy required to deform the sample for the next ones [23]. The variation of the relative strain energy for NBR-100 and NBR-200 without NP was comparable. With aqueous nTiO₂, the energy required to deform the sample is less important because the elastomer membrane is weakened by its swelling [24]. As shown before, NBR-100 swells more than NBR-200 for a same immersion time. This explains the difference between both plateaus obtained with nTiO₂ in water. It is observed that the strain energy is low when the swelling of the sample is important.
5. Conclusion

This paper has investigated the penetration of nTiO$_2$ in water through nitrile protective gloves that were subjected to BD, corresponding to soft conditions of occupational use. The penetration of nTiO$_2$ was recorded for disposable nitrile gloves exposed to aqueous nTiO$_2$ after 5 and 7 hours. This penetration of the NPs through the protective material was attributed in part to a degradation of its physical and mechanical properties following repetitive mechanical deformations and contact with aqueous nTiO$_2$. Moreover, to simulate realistic work conditions encountered by protective gloves, new tests were performed. They consist in one 50%-BD applied per minute during the experiment duration (3 hours corresponding to 180 BD). These conditions increase the physical degradation of the glove samples which should further facilitate the penetration of NPs through protective gloves. In conclusion, the results presented show that great care must be exercised when selecting protective gloves for the handling of NPs. Even if more work is needed to confirm these worrying results, it is however already possible to recommend a frequent replacement of disposable gloves in case of exposure to NPs, especially when exposure of the NPs occurs in the liquid phase.

Acknowledgements

The authors would like to acknowledge the contribution of G. Perron, M. Ben Salah, J. De Santa Barbara (École de technologie supérieure) to the project as well as the contribution of Madjid Hadioui (Université de Montréal).

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