Research Article

Swelling of Elastomers in Solutions of TiO₂ Nanoparticles

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Elastomers used in protective gloves can be sensitive to the action of solvents used to disperse commercial solutions of nanoparticles. These effects may include the swelling of the polymer, leading to a modification of its mechanical and chemical properties. Modifications to the properties of the polymer will impact the protection provided by the protective gloves. The goal of this work was therefore to study the swelling of several elastomers when exposed to commercial solutions of nanoparticles. The study involved four elastomers and three commercial solutions of colloidal titanium dioxide (TiO₂). Swelling was assessed by measurements of mass gain and length change. Tests were also performed with technical and ultrapure solvents corresponding to the liquid carriers. The solutions had a significant effect on the swelling of nitrile rubber, latex, and neoprene. A large mass gain was recorded for short immersion times, indicating a possible penetration of the nanoparticle liquid carrier into these elastomers. Length change measurements revealed a swelling anisotropy effect with nitrile rubber and latex in the solutions of colloidal TiO₂. No effect was measured with butyl rubber. The results show that great care must be taken when selecting protective gloves for the handling of nanoparticle dispersions.

1. Introduction

Titanium dioxide nanoparticles (nTiO₂) are now manufactured and used in several commercial products such as paints, varnishes, and sunscreens [1, 2]. If their use seems inevitable, more and more studies are signaling that they may have harmful effects on health, especially for workers and researchers. Indeed, studies conducted on rats and mice that were exposed by intratracheal instillation to either 250 nm TiO₂ and 20 nm nTiO₂ reported an inflammatory response [3–5] that was higher for the nTiO₂. Another study showed a small increase in the number of cancers found among workers who were in contact with nTiO₂ [6]. According to these results, the International Agency for Research on Cancer (IARC) classified titanium dioxide in 2B-group as possibly carcinogenic to humans [7]. This has led several government agencies to recommend application of the precautionary principle [8, 9]. This includes the use of protective gloves against chemicals, even if no thorough scientific validation of their efficiency has been made, under conditions relevant to the use of nanomaterials under a typical occupational setting.

Titanium dioxide nanoparticles are manufactured and distributed in several forms, which include powders and colloidal solutions. In fact, for safety purposes, an increasing number of manufacturers favour the distribution of nanoparticles in solution in order to limit the risks due to aerosolization and inhalation [10]. However, the elastomers used in protective gloves can be sensitive to solvents and they may sustain significant swelling as well as degradation [11, 12]. The level of the effect depends on numerous parameters including the formulation of the polymer and the nature of the solvent. In the case where solvents are used to disperse the nanoparticles, there is a risk that they facilitate the passage of nanoparticles through the protective gloves.

Several studies have examined the swelling behaviour of polymers in solvents. For example, Perron et al. (2002) measured the swelling of different protective glove materials in more than fifty solvents [13]. Golanski et al. (2010) followed the diffusion of tritiated water through nitrile

rubber, latex, and vinyl gloves [14]. In each case, effects on the gloves were recorded after five days or less. A diffusion coefficient of $5 \cdot 10^{-12}$ m^2/s was measured for nitrile rubber and $3 \cdot 10^{-13}$ m^2/s for latex.

This paper examines the swelling of protective glove elastomers (disposable nitrile rubber and latex, and nondisposable neoprene and butyl rubber) in the liquid carriers and commercial solutions typically used to disperse nanoparticles (in this case, 15 nm nTiO$_2$). The results are discussed with respect to the potential protective effect of the gloves to nanoparticle suspensions.

2. Materials

2.1. Elastomers. Five models of protective gloves corresponding to four types of elastomers were selected for this study: two disposable nitrile rubber gloves (Best Nitrile Care 3005-PFL, 100 μm thick), disposable latex gloves (Ansell Conform XT 69-318, 100 μm thick), nonsupported neoprene gloves (Ansell Neoprene 29-865, 450 μm thick), and non-supported butyl rubber gloves (Best Butyl 878, 700 μm thick). The difference between the two types of nitrile rubber gloves is related to the fact that one is labelled by the manufacturer as containing no silicone, no plasticizer, and no filler. In this paper, results for this glove model will be identified as nitrile rubber T-N-T.

2.2. Commercial nTiO$_2$ Solutions. Three nanoparticle suspensions were used for this study. All three contained 15 nm anatase titanium dioxide nanoparticles. The aqueous nTiO$_2$ (15% w/w) and the nTiO$_2$ in 1,2-ethanediol (EG, 20% w/w) were obtained from Nanostructured & Amorphous Materials, Inc. (Houston, TX, USA). A 20% (w/w) solution in 1,2-propanediol (PG) was purchased from MK Impex (Mississauga, ON, Canada). Particle sizes of 21 ± 2 nm (for nTiO$_2$ in water) and 24 ± 3 nm (for nTiO$_2$ in EG) were measured by fluorescence correlation spectrometry (FCS) [15]. The same analysis was not possible for nTiO$_2$ in PG due to an incompatibility with the FCS measurement cells.

2.3. Technical Grade and Ultrapure Solvents. Technical grade and ultrapure solvents corresponding to the nTiO$_2$ carriers were obtained for comparison purposes. 1,2-ethanediol and 1,2-propanediol were purchased from Fisher Scientific; ultrapure solvents anhydrous 1,2-ethanediol (99.8% w/w) and 1,2-propanediol (99.5% w/w) were obtained from Sigma Aldrich. Water was obtained from a laboratory distillation system or purchased from Acros Organics (HPLC grade).

3. Experimental Protocol

A series of experiments were performed to characterize the colloidal solutions and the solutions where elastomer samples were immersed. Firstly, 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°C with a step of 5°C/min. Secondly, 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. To determine the presence or not of residues in solvents, FT-IR analysis was complemented by Energy-dispersive X-ray spectroscopy (EDS, JEOL JEM-2100F). To obtain statistically significant data, triplicate measurements were performed for all tests.

Swelling can be quantified by measuring the polymer mass gain and/or length change as a function of time [13]. Both mass and length gain measurements were performed on a small rectangular sample (dimensions: 10 mm × 50 mm for measurements of mass; 4 mm × 50 mm for length measurements). All samples were taken from the palm section of the gloves. For each test, three to five replicates were measured in order to obtain statistically significant data. Samples were immersed in either the commercial solutions of nTiO$_2$ or in the technical/ultrapure solvents. At regular intervals, samples were removed from the liquid, gently dried with a paper towel before being weighed on an analytical balance (±0.1 mg) or measured using a vernier caliper (±0.01 mm). In order to minimize the effect of elastomer porosity on the mass measurement, the reference value was obtained following the immersion of the sample in either the colloidal solution or the solvents where the mass gain and length change were defined as

$$\Delta X(t) = \frac{X_t - X_{0+}}{X_{0+}} \tag{1}$$

with X_t being the mass or length at time t and X_{0+} the corresponding reference value.

It is also possible to estimate diffusion coefficients through the polymer from the temporal variations of mass or length. Based on Fick's first law, the ratio between the mass or length at time t and that at infinite time (i.e., maximum swelling) is given by [13]

$$\frac{X_t}{X_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{m=\infty} \frac{1}{(2m+1)^2} \left\{ \exp\left(-D \frac{(2m+1)^2 \pi^2}{e^2} t \right) \right\}, \tag{2}$$

where D is the diffusion coefficient ($m^2 \cdot s^{-1}$) and e the sample thickness.

Equation (2) can be simplified by considering that the exponential term decreases quickly with m. A half-life time ($t_{1/2}$) is obtained for a mass or a length ratio equal to 0.5:

$$\frac{X_t}{X_\infty} \cong 1 - \frac{8}{\pi^2} \left\{ \exp\left(-D \frac{\pi^2}{e^2} t_{1/2} \right) \right\} = 0.5. \tag{3}$$

The value of $t_{1/2}$ can be determined from the linear regression of $(X_t - X_0)/(X_\infty - X_0)$ as a function of the square root of

time for a value of $(X_t - X_0)/(X_\infty - X_0) = 1/2$. The diffusion coefficient can be estimated from (5):

$$\frac{X_t - X_0}{X_\infty - X_0} = f\left(\sqrt{t}\right), \tag{4}$$

$$D \approx \frac{0.04919e^2}{t_{1/2}}. \tag{5}$$

4. Results and Discussion

4.1. Analysis of Nanoparticle Solutions. In Figure 1, the variation of the relative mass loss is shown as a function of temperature for the aqueous solution of $nTiO_2$ and for two slightly different qualities of water (distilled water and ultra-high purity water). The distilled water and ultra-high purity water curves overlapped exactly, indicating negligible chemical contamination. On the other hand, the curve for the aqueous solution of $nTiO_2$ was shifted slightly towards higher temperatures. The same phenomenon was observed when comparing the curves obtained for $nTiO_2$ in PG (data not shown) with technical grade and ultrapure PG. In the case of $nTiO_2$ in EG, the same shift in temperature was observed, however, the curves corresponding to technical and ultrapure EG did not overlap, indicating a difference in composition between the two products. In all cases, the observed shift towards a higher temperature was attributed to the presence of the $nTiO_2$ to which the solvent molecules adsorb, thus increasing the vapour pressure of the system [16]. The similarity in the profiles in the absence or presence of $nTiO_2$ is consistent with the absence of significant quantities of additives (at least below the detection limits of the thermogravimetric technique). Moreover, in the aqueous stock solution, a value of $(14.3 \pm 0.8)\%$ w/w was obtained for the concentration of the $nTiO_2$. For the $nTiO_2$ in EG and PG, the measured mass ratios were, respectively, $(16.1 \pm 0.1)\%$ w/w and $(25.0 \pm 3.7)\%$ w/w. These values were very close to indications that were provided by the manufacturers. Colloidal solutions often contain additives such as stabilizing agents which may affect polymer swelling. Therefore, the TGA spectra for the colloidal solutions were compared with those obtained for the technical grade and ultra-high purity solvents corresponding to the liquid carriers.

Figure 2 shows the FT-IR spectra obtained for the $nTiO_2$ in water and in ultra-high purity water. In the presence of the $nTiO_2$, an additional peak was observed at $1070 \, cm^{-1}$. This peak is generally associated with the elongation of a CO bond, which may indicate the presence of an additive, such as an alcohol, in the $nTiO_2$ solution [16]. On the other hand, no significant differences were observed between the spectra of $nTiO_2$ in EG or PG and the corresponding ultrapure solvents. Nonetheless, these spectra were admittedly complex, which made it extremely difficult to detect any additional peaks associated with additives. Furthermore, it could not be excluded that peaks corresponding to the additives were masked by the characteristic peaks of the two glycols.

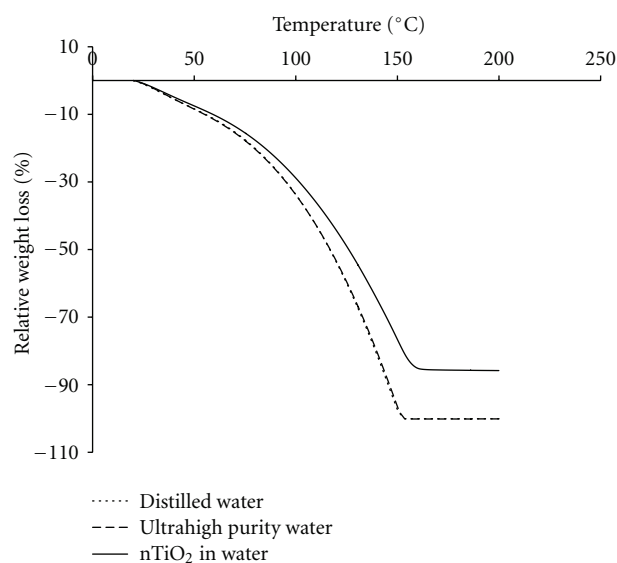*4.2. Swelling Measurements (Mass Gain).* Swelling measurements were made by recording the mass of glove material

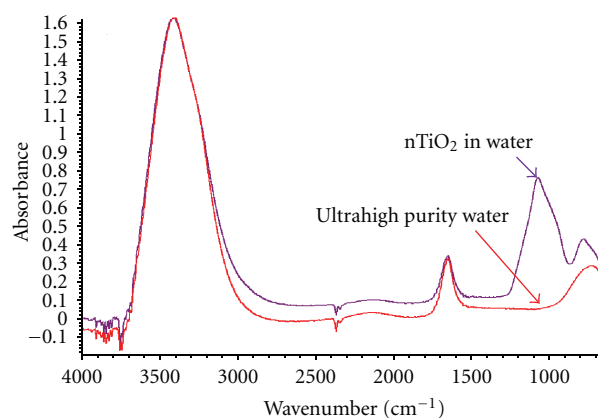FIGURE 1: TGA spectra of $nTiO_2$ in water, distilled water, and ultra-high purity water.

FIGURE 2: FT-IR spectra of $nTiO_2$ in water and ultra-high purity water.

samples after immersion in the $nTiO_2$ solutions. The results obtained for nitrile rubber immersed in the $nTiO_2$ in water over 8 hours are displayed in Figure 3. A steady increase in mass was observed. In order to verify if mass gain was due to an accumulation of the nanoparticles [17], swelling measurements were also conducted in the ultrapure solvents, corresponding to the $nTiO_2$ carriers. In this case, the curve obtained for the ultra-high purity water was extremely well superimposed on that obtained for the $nTiO_2$ in water (Figure 3), strongly suggesting that the mass gain could be attributed solely to a swelling of the nitrile rubber by the solvent.

In order to ensure that these results were representative of the behaviour of disposable nitrile rubber gloves, they were compared with the swelling behaviour of a model T-N-T glove, which, according to the manufacturer, contains no silicone, no plasticizer and no filler. Results were presented for a 5-hour immersion in ultra-high purity water (Figure 4).
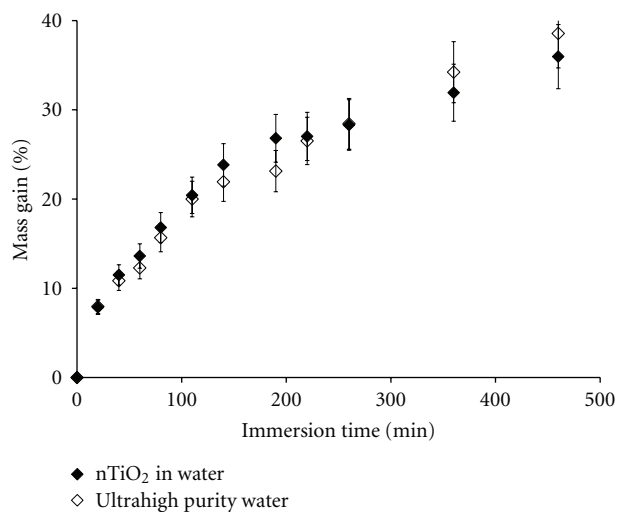
Figure 3: Variation of mass gain for nitrile rubber as a function of immersion time in nTiO$_2$ in water. Error bars correspond to standard deviations obtained from 3 measurements.
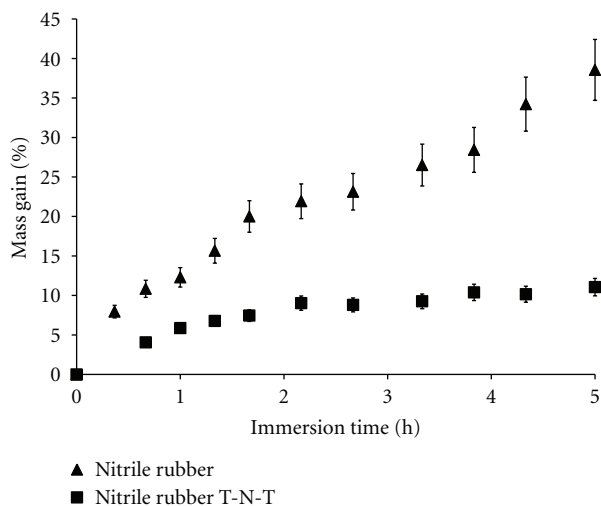

Figure 4: Variation of mass gain as a function of immersion time in ultra-high purity water for nitrile rubber and nitrile rubber T-N-T samples.

Figure 5: Variation of mass gain of a nitrile rubber sample as a function of immersion time for the nTiO$_2$ in water, PG, and EG.

In spite of a similar trend in the data, a significant difference in amplitude was observed between the two nitrile rubber gloves. The mass gain reaches about 38% for the filler-containing gloves and only 10% for the T-N-T gloves. Nonetheless, nitrile rubber gloves showed substantial swelling in water, both in the presence and absence of filler.

The swelling behaviour of the nitrile rubber in the two other nTiO$_2$ solutions was also investigated. The mass gain of the nitrile rubber samples was presented as a function of immersion time in water, EG, and PG containing nTiO$_2$ (Figure 5). A gradual mass increase was observed for all of the colloidal solutions, with virtually identical data for the EG
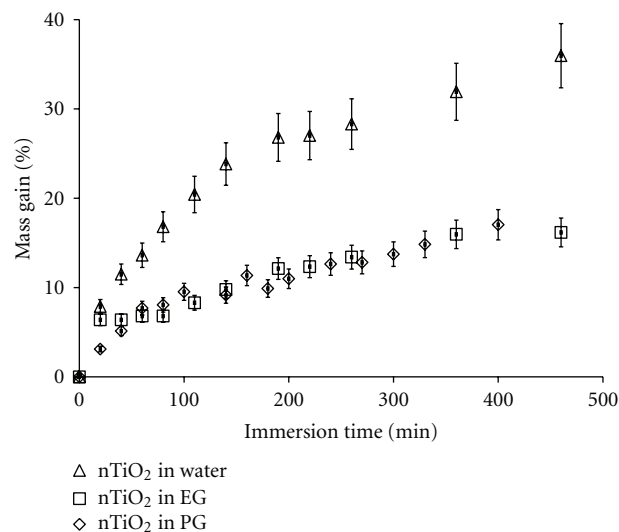
and PG solutions. Such a result is not surprising, given that EG and PG are chemically similar and the chemical family of the solvent is one of the primary parameters controlling elastomer swelling [11]. The swelling ratio of the nitrile rubber in the aqueous nTiO$_2$ solution was about 3x higher than that observed in EG/PG. For example, for an immersion time of 8 hours, the swelling ratio for nitrile rubber in the nTiO$_2$ in water was 35%, while it was 15% for nTiO$_2$ in the other carriers. The differences are attributed to differences in viscosity, molecule size and structure and polarity between the two solvent families [16]. Nonetheless, it should be noted that maximum swelling was not reached for any of the nTiO$_2$ solutions even after 8 hours of immersion.

Swelling behaviour of the four glove materials was analysed for each of the nTiO$_2$ samples in water, EG, and PG over 3 days (Figure 6). Some major differences in swelling behaviour were observed among the four elastomers. For example, the mass gain for nitrile rubber reached about 79% after 3 days of immersion while it attained 27% for the latex and 18% for the neoprene. For the all three elastomers, the variation in mass gain started immediately following the immersion of the samples in the nTiO$_2$ solutions, but was fairly gradual, taking about 40 hours to reach steady state. In the case of butyl rubber, no significant mass gain was recorded.

The maximum mass ratio values that were measured for each of the four glove materials and three nTiO$_2$ solutions are given in Table 1. In summary, swelling appeared to depend more on the glove elastomers than it did on the solvent. In all of the carrier phases, nitrile rubber showed the greatest swelling, whereas latex and neoprene gave an intermediate response. No swelling of butyl rubber was observed in any of the three nTiO$_2$ suspensions.

The mass gain was attributed to the diffusion of solvent molecules into the polymer membrane. Using the mass gain data and (5), diffusion coefficients of the three solutions
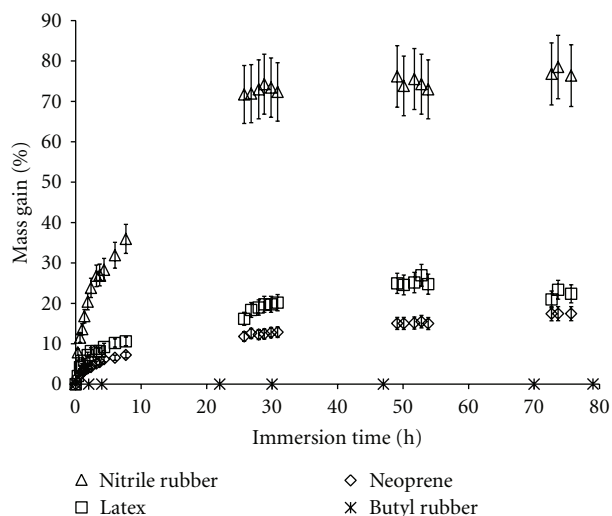
FIGURE 6: Variation of mass gain as a function of immersion time in nTiO$_2$ in water for nitrile rubber, neoprene, and latex samples.

TABLE 1: Values of maximal swelling ratio for the four glove materials in the three nTiO$_2$ solutions.

	Maximum mass change ratio (%)		
	nTiO$_2$ in water	nTiO$_2$ in EG	nTiO$_2$ in PG
Nitrile rubber	79	73	94
Latex	27	14	26
Neoprene	18	11	11
Butyl rubber	0	0	0

(water, PG, and EG) into the nitrile rubber, latex, and neoprene were estimated. The diffusion coefficient was not calculated for butyl rubber since no mass change was recorded. As can be seen in Table 2, the three nTiO$_2$ carriers diffused more rapidly into neoprene than in latex and nitrile rubber. Note that, in addition to the composition of the glove, diffusion coefficient determinations also take into account its thickness. The values suggest that the neoprene would only provide a moderate resistance to chemicals, whereas nitrile rubber and latex showed a similar resistance. Significant differences between the three carrier solutions were also observed. Indeed, for all three glove materials, water diffused faster than EG, which diffused faster than PG. The differences in viscosity, molecule size, and polarity between the two solvent families explain that water diffused faster than glycols [16]. Nonetheless, values are substantially lower than what has been measured previously with more efficient solvents (e.g., D for toluene in latex = 11.4 $\times$ 10^{-11} m$^2 \cdot$s^{-1}); [13].

4.3. Length Change Measurements.

The swelling of the elastomers was also characterized by measurements of length variations. For example, length change is presented over 10 days for the nitrile rubber immersed in the nTiO$_2$ in EG or in ultrapure EG (Figure 7). To obtain statistically significant data, triplicate measurements were performed for each test.

TABLE 2: Diffusion coefficients of the three nTiO$_2$ carriers in nitrile rubber, latex, and neoprene. Values were obtained by mass gain based upon (5).

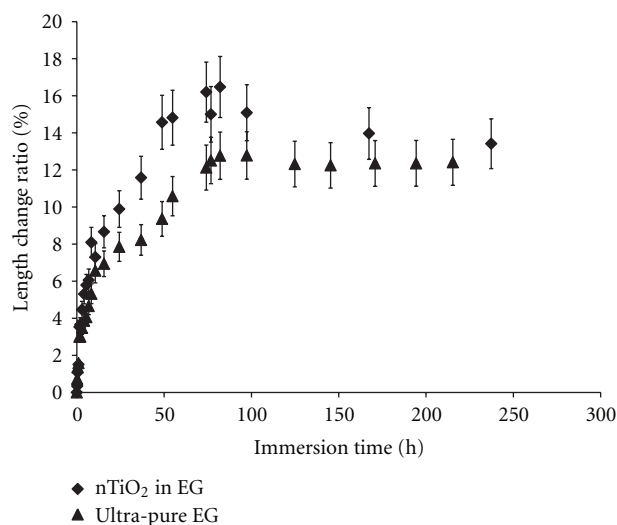|	Diffusion coefficients (10^{-14} m$^2 \cdot$s^{-1})		
	Water	EG	PG
Nitrile rubber	1.6	0.7	0.5
Latex	1.4	1.4	0.4
Neoprene	10.4	6.9	1.5

FIGURE 7: Variation of length change ratio as a function of immersion time in nTiO$_2$ in EG and in ultrapure EG for nitrile rubber sample.

A gradual increase in sample length was observed, with a constant length value found after 85 hours, reasonably consistent with determinations of mass gain. In the nTiO$_2$ in EG, the length increased by a maximum of 16% while it increased by 13% for the ultrapure EG. This difference was attributed to the possible presence of additives (or eventually the nTiO$_2$ itself) in the nTiO$_2$ solution.

Length changes were compared in the three different nTiO$_2$ carriers (Figure 8). Swelling strongly depended on the solutions in which the elastomer is immersed. For example, the nitrile rubber attained its maximum length (+16%) after only 85 hours in EG while it took 500 hours (20 days) to reach the same maxima when the immersion was performed in PG. When the immersion was performed in the nTiO$_2$ in water, the maximum length was observed around 85 h, but the increase was only 10%, substantially less than the results for the two solvents in the glycol chemical family.

The swelling of the three glove materials was compared following their immersion in the nTiO$_2$ in PG (Figure 9). Large differences were observed among the three materials. For example, while the maximum length change for both the nitrile rubber and the neoprene was attained after about 500 h (20 days) of immersion, it was only +16% for the nitrile rubber, whereas it was +5% for the neoprene. Surprisingly, for the latex, the maximum length change ratio
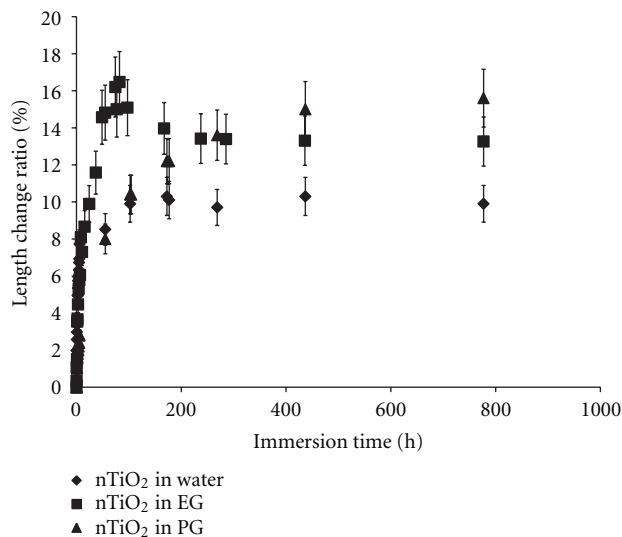
FIGURE 8: Variation in length change ratio of a nitrile rubber as a function of immersion time for the nTiO$_2$ in water, PG, and EG.

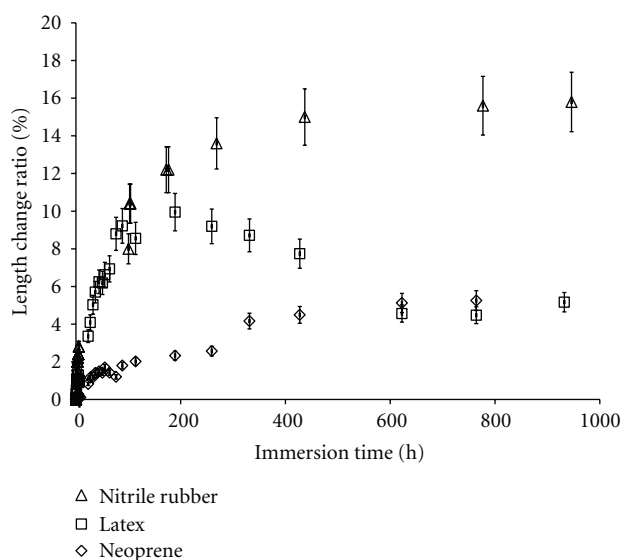FIGURE 9: Variation in length change ratio as a function of immersion time in nTiO$_2$ in PG for nitrile rubber, neoprene and latex samples.

TABLE 3: Maximal values of length change for the nitrile rubber, neoprene, and latex glove materials in the three solutions of nTiO$_2$.

	Maximum length change ratio (%)		
	Water	EG	PG
Nitrile rubber	10.3	16.5	15.8
Latex	7.3	8.1	9.9
Neoprene	10.0	2.7	5.3

TABLE 4: Diffusion coefficients of the three TiO$_2$ solutions for nitrile rubber, latex, and neoprene obtained by measured changes in length of the elastomers.

	Diffusion coefficients (10^{-14} m$^2 \cdot$s^{-1})		
	nTiO$_2$ in water	nTiO$_2$ in EG	nTiO$_2$ in PG
Nitrile rubber	4.3	0.9	0.2
Latex	2.4	0.7	0.7
Neoprene	4.1	4.0	1.4

measured length changes Table 4. Although these values are slightly different than those obtained with the mass gain, the same tendency can be observed. Water diffused faster than EG, which diffused faster than PG.

Length data obtained above was determined on samples cut in a perpendicular (transverse) direction to the glove fingers. Comparison of measurements carried out for transverse and longitudinal cuts of the nitrile rubber samples showed a significant difference in the lengths in PG with a maximum increase of 7% in the traverse direction as opposed to 2% in the longitudinal orientation (Figure 10). More work is needed to fully understand and characterize this phenomenon, however, may be related to the glove manufacturing process by dipping.

4.4. Degradation of the Gloves. Analysis of the swelling solutions was performed by FT-IR (Fourier transform Infrared Spectroscopy) and EDS (Energy Dispersive Spectroscopy). Neoprene samples were immersed for 7 days in water, EG, and PG. Solutions were initially colourless but had a yellow colour after 7 days. A drop of solution was deposited on a microscope slide and the solvent evaporated so that residues could be analysed. For the EG sample, FT-IR spectrum showed peaks at 3342 cm^{-1}, 1029 cm^{-1}, and 2935 cm^{-1}, likely corresponding to the C-O and C-H bonds of the EG (Figure 11). On the other hand, the peak observed at 754 cm^{-1} is more characteristic of N–H bonds, which could indicate the presence of an amine in the swelling solution, for example, diaminodiphenylmethane, which is used as a vulcanizing agent in the manufacture of neoprene gloves [18], or phenylenediamine, which is used as an antioxidant in neoprene gloves [19]. In addition, the peak around 1600 cm^{-1} can be associated with chlorine, a lateral group in the chemical structure of neoprene. The FT-IR analysis was complemented by EDS analysis of the same residues. Peaks associated with zinc, calcium, chlorine, sulphur, aluminium, magnesium, and sodium were observed. Magnesium and zinc oxides are typically used as vulcanization agents,

was reached after only 200 hours (+10%); however, the length change subsequently decreased to 5% at the full term of the experiment. The reduction in length at the longer periods of immersion was attributed to a degradation of the glove material in the PG. Maximum length change values, measured for the nitrile rubber, neoprene, and latex in all three nTiO2 solutions, are given in Table 3. Measurements were not performed for the butyl rubber due to the absence of mass change recorded above. For all of the carriers, the largest relative change in length was recorded for the nitrile rubber, similar to the results obtained for mass gain.

Diffusion coefficients were determined in each of the glove materials, for each of the three solutions, using the
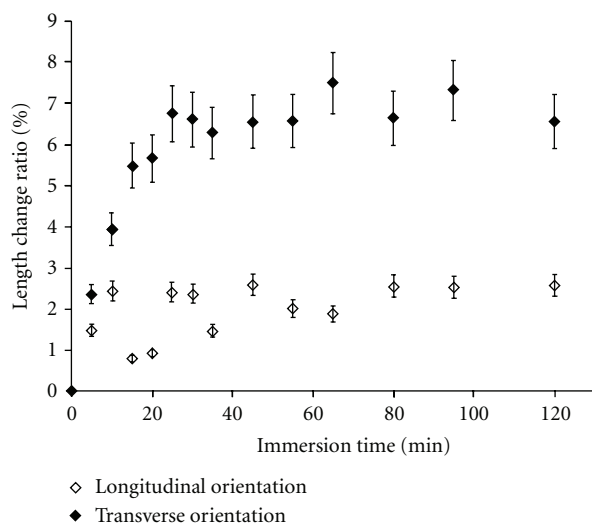
FIGURE 10: Variation in length change ratio as a function of immersion time in PG for transverse and longitudinal nitrile rubber samples. Error bars correspond to standard deviations obtained from 3 measurements.

FIGURE 12: Variation in the concentration of titanium in the sampling solutions as a function of the duration of 50% biaxial deformations for nitrile (NBR) and butyl (IIR) rubber samples exposed to colloidal solutions of $nTiO_2$.
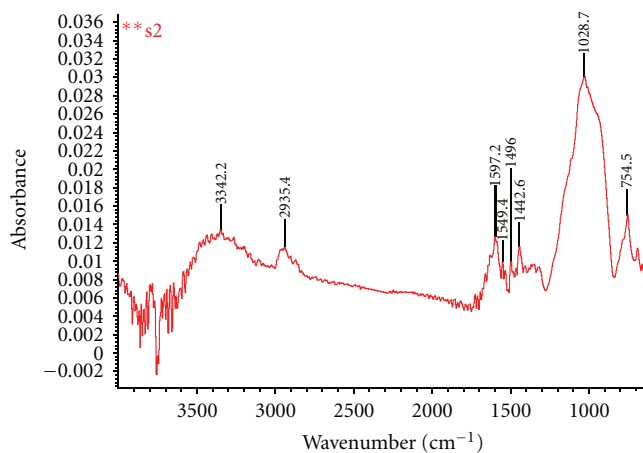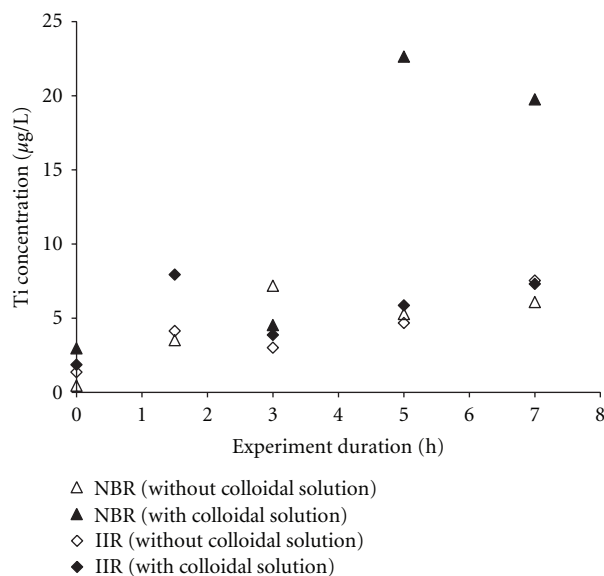

FIGURE 11: FT-IR spectrum of the swelling residues from neoprene immersed for 7 days in EG.

whereas sulphur is used as a vulcanization catalyst [18]. For their part, calcium and aluminium particles are used as fillers. The results indicate that, in parallel to the diffusion of the solvents into the glove materials, some chemical species are extracted at long immersion times. These leached-out species include vulcanization agents and catalysts, antioxidants, reinforcing particles, and nonpolymerised monomers. The extraction of these compounds may affect the physical and mechanical properties of the elastomer membrane [20].

4.5. Implications for the Protection against Nanoparticle Exposure. As studied by Vinches et al. (submitted, July 2012), 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 (Figure 12). No differences were observed for

measurements made with and without the NPs for the samples composed of butyl rubber [21]. The swelling of gloves materials, in this case for nitrile rubber, is one of the phenomena which can facilitate the penetration of $nTiO_2$ solutions through protective gloves.

5. Conclusion

This paper has investigated the swelling of elastomers used in protective gloves upon their exposure to commercial solutions of nanoparticles. Results were obtained for the swelling of four glove materials—nitrile rubber, neoprene, latex and butyl rubber—exposed to three commercial solutions of $nTiO_2$ (water, 1,2-ethanediol, and 1,2-propanediol (PG). Comparisons were made with technical and ultra-pure solvents that corresponded to the nanoparticle carriers over short- and long-term experiments. Complementary analysis of the carriers was performed by TGA and FTIR; analysis on the residues in the carriers after a 7 day exposure of the gloves was performed by EDS and FTIR. Results showed that the solutions had a significant effect on the swelling of nitrile rubber, latex, and neoprene. In contrast, no significant swelling of butyl rubber was observed for any of the $nTiO_2$ carriers. Indeed, a large mass gain was recorded for short immersion times (within a few hours), indicating penetration of the nanoparticle carrier solutions into the elastomers. Mass and length measurements gave comparable values for the diffusion coefficients. The largest diffusion coefficients were obtained for neoprene, which indicated a larger sensitivity to the $nTiO_2$ carriers. In some instances, a decrease in the elastomer mass and length was observed for long immersion times, although the decrease occurred for times which were generally much longer than a typical

period for glove renewal. This phenomenon was attributed to the leaching of additives from the gloves.

These results show that great care must be taken in selecting protective gloves for the handling of nanoparticles in colloidal solutions. Indeed, given the carrier solutions diffuse through the glove, the transport of the nanoparticles themselves can be facilitated, thus allowing for exposure to the skin.

Acknowledgments

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