

Swelling of Protective Gloves in Commercial TiO₂ Nanoparticles Colloidal Solutions

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Abstract– Titanium dioxide (TiO₂) nanoparticles enter in the composition of numerous manufactured products such as sunscreens or paints for example and their use seems today inescapable. Some of them are delivered in colloidal solutions to reduce aerolization risks. However, elastomers used in the manufacture of protective gloves may be sensitive to the action of solvents employed as liquid carriers in these commercial nanoparticles solutions. Effects may involve the swelling of the polymer by the solvent. If the solvent emerges on the inner side of the protective glove, it may carry nanoparticles with it, thus facilitating their penetration through gloves. This work aims at studying the swelling of four elastomers used in protective gloves when immersed in TiO₂ colloidal solutions as well as in technical and ultra-pure solvents corresponding to the liquid carriers used in the nanoparticles solutions. The study involves latex, neoprene, nitrile and butyl rubber gloves and three commercial TiO₂ colloidal solutions in water, 1,2-propanediol and 1,2-ethanediol. The swelling behaviour was assessed by mass gain and length change measurements. It was observed that the studied solutions have a significant swelling effect on nitrile rubber, latex and neoprene. On the other hand, no effect was measured with butyl rubber. As revealed by the non-negligible swelling recorded even for short immersion times, a possibility exists for a liquid carrier-mediated penetration of TiO₂ nanoparticles through these protective gloves. These results are in agreement with preliminary measurements showing by chemical analysis of sampling solutions a possible

penetration of TiO₂ nanoparticles through gloves when in colloidal solutions. This demonstrates that great care must be taken when selecting protective gloves for handling nanoparticles in solutions.

Keywords: Swelling, Colloidal Solutions, Titanium Dioxide Nanoparticles, Protective Gloves, Diffusion Coefficient

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1. Introduction

Nanoparticles, particularly titanium dioxide nanoparticles (nTiO₂), are increasingly present in several commercial products like paints, varnishes, sunscreens, etc. (Hervé-Bazin 2007; Robichaud et al. 2009). More and more studies caution about their likely harmful effects on health, especially for workers and researchers. For example, a small increase in the number of cancer among workers in contact with nTiO₂ have been reported (C.C.H.S.T. 2007). Moreover, studies conducted on rats and mice, which were exposed to 250 nm TiO₂ pigment and 20 nm nTiO₂ instilled by intratracheal, recorded the occurrence of pulmonary effects

(Höhr et al. 2002; Warheit et al. 2006; Warheit et al. 2007). The observed inflammatory response was higher with nTiO₂.

Based on these results, the International Agency for Research on Cancer (I.A.R.C.) has classified nanosized titanium dioxide in 2B-group as possibly carcinogenic to humans (I.A.R.C. 2010). In response to this classification, several Health & Safety government agencies have recommended the application of the precautionary principle (Ostiguy et al. 2009; OECD 2010). One of their recommendations is the use of protective gloves against chemicals, even if no thorough scientific validation of their efficiency against nanoparticles has been made yet.

To reduce aerolization risks for safety purposes, an increasing number of manufacturers offer nanoparticles in solutions instead of powder (Bordere et al. 2011). However, as shown by Nohilé et al. (2008, 2010), elastomers used in protective gloves are sensitive to solvents and may sustain significant swelling as well as degradation. The swelling phenomenon can be quantified by measuring the polymer mass gain versus time, allowing the computation of solvent diffusion coefficient values (Perron et al. 2002).

The swelling behaviour of polymers in solvents has already been largely documented by Hansen solubility parameters and his HSPiP application (Hansen 2000). For example, Perron et al. measured the swelling of different protective glove materials in more than fifty solvents (Perron et al. 2002). For their part, Golanski et al. studied the diffusion of tritiated water through three elastomers used in protective gloves, nitrile rubber, latex and vinyl (Golanski et al. 2010). For all of them, water diffusion through the samples was recorded within five days or less. For nitrile rubber, a value of diffusion coefficient of about 5.10^{-12} m²/s was measured and 3.10^{-13} m²/s for latex.

Since solvents are used as liquid carriers in nanoparticles solutions, this raises the risk that they facilitate the passage of nanoparticles through protective gloves. As preliminary results have shown, a significant swelling of various protective glove materials in commercial nTiO₂ solutions may occur (Dolez et al. (2010), Vinches et al. (2011)). For example, a 4% length change was observed for nitrile rubber after only 2 hours of immersion time in a commercial nTiO₂ solution in water and a 35% mass gain was measured after 8 hours.

This paper provides a more in-depth study of the swelling effect of elastomer protective gloves - disposable nitrile rubber and latex, and non-supported neoprene and butyl rubber - in 15 nm nTiO₂ commercial solutions.

2. Materials

2.1. Elastomers

For this study, five models of protective gloves corresponding to four types of elastomers were used: two disposable nitrile rubber gloves to compare the effect of the thickness (Best Nitrile Care 3005-PFL, 100 µm thick and Best Nitrile Care 8005-PFL, 200 µm), disposable latex gloves

(Ansell Conform® XT 69-318, 100 µm thick), non-supported neoprene gloves (Ansell Neoprene 29-865, 450 µm thick) and non-supported butyl rubber gloves (Best Butyl 878, 700 µm thick). Unless otherwise specified, nitrile rubber samples correspond to Best Nitrile Care 3005-PFL glove model.

2.2. Commercial TiO₂ Colloidal Solutions

Three types of nanoparticles solutions were selected for the swelling tests. They all contain 15 nm, anatase titanium dioxide nanoparticles. nTiO₂ solutions in water (15 wt%) and 1,2-ethanediol (EG, 20 wt%) were obtained from Nanostructured & Amorphous Materials, Inc. (Houston, TX). A 20 wt% colloidal solution in 1,2-propanediol (PG) was purchased from MK Impex (Mississauga, ON). Particle sizes of 21 ± 2 nm (for nTiO₂ in water) and 35 ± 3 nm (for nTiO₂ in EG) were measured by fluorescence correlation spectrometry (FSC). The same analysis was not possible for nTiO₂ in PG due to an incompatibility between the cell material and the colloidal solution liquid carrier.

2.3. Technical Grade and Ultra-Pure Solvents

Technical grade and ultra-pure solvents corresponding to the commercial colloidal solution liquid carriers were also obtained for comparison purposes. The ultra-pure solvents are anhydrous 1,2-ethanediol (99.8 wt%) and reagent 1,2-propanediol (99.5 wt%) from Sigma Aldrich and HPLC water from Acros Organics. Technical solvents are 1,2-ethanediol and 1,2-propanediol (Fisher Chemicals), and laboratory-made distilled water.

3. Experimental Setup

Mass gain measurements were performed on 4 x 50 mm rectangular samples taken from the palm section of the gloves. To obtain statistically significant data, three replicates were produced for each test. The measurements were performed by immersing the samples in the commercial nTiO₂ solutions or in technical/ultra-pure solvents. At regular intervals, samples were removed from the liquid, their surface gently wiped with a paper towel before being weighed using a precision balance (± 0.1 mg). The mass gain was computed using the following expression:

$$\Delta M(t) = \frac{M_t - M_0}{M_0} \quad (1)$$

With M_t being the mass at time t and M_0 the corresponding value before immersion.

Using the data corresponding to the variation of the mass of the sample as a function of the immersion time, it is possible to estimate the corresponding value of diffusion coefficient. Indeed, according to Fick's first law, Eq. (2) was derived relating the ratio between the mass at time t and at infinite time (i.e. at maximum swelling) and mostly used (Perron et al. 2002):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{m=\infty} \frac{1}{(2m+1)^2} \left\{ \exp \left(-D \frac{(2m+1)^2 \pi^2}{e^2} t \right) \right\} \quad (2)$$

With D the diffusion coefficient and e the sample thickness.

Eq. (2) can be simplified considering that the exponential term decreases quickly with m . A half-life time ($t_{1/2}$) is obtained for a mass ratio equal to 0.5 as shown in Eq. (3):

$$\frac{M_t}{M_\infty} \cong 1 - \frac{8}{\pi^2} \left\{ \exp \left(-D \frac{\pi^2}{e^2} t_{1/2} \right) \right\} = 0,5 \quad (3)$$

The value of $t_{1/2}$ is provided at $(M_t - M_0)/(M_\infty - M_0) = 1/2$ by fitting the data expressed according to Eq. (4) by a linear regression. The diffusion coefficient is given by Eq. (5).

$$\frac{M_t - M_0}{M_\infty - M_0} = f(\sqrt{t}) \quad (4)$$

$$D \approx \frac{0,04919 e^2}{t_{1/2}} \quad (5)$$

The experimental setup for length change measurements was the same as described for the mass gain measurements. However, in that case, the length of the sample was measured with a vernier calliper (± 0.01 mm). The length change ratio was computed using Eq. (1) by replacing mass data by length data.

4. Results and Discussion

4. 1. Analysis of the Colloidal Solutions by Infrared Spectroscopy

Colloidal solutions usually contain additives such as stabilizing agents which may affect the swelling phenomenon. A comparison of the nTiO₂ solutions with the corresponding technical grade and ultra-high purity solvents was performed by infrared spectroscopy (FT-IR, Nicolet Continuum XL). Measurements were made in attenuated total reflectance (ATR) mode on drops of solutions after almost total evaporation of the solvent. As it can be observed in Fig 1, an additional peak appears at 1070 cm⁻¹ for the nTiO₂ solution in water compared to the spectrum of ultra-high purity 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 nTiO₂ solution. On the other hand, the spectra of colloidal solutions in EG or PG and the corresponding ultra-pure solvents do not disclose any significant difference. In these cases, spectra exhibit a complex structure which may explain the difficulty in detecting additional peaks associated with the presence of additives. Moreover, the characteristic peaks of these additives might be superimposed with those of the two glycols, thus preventing their detection.

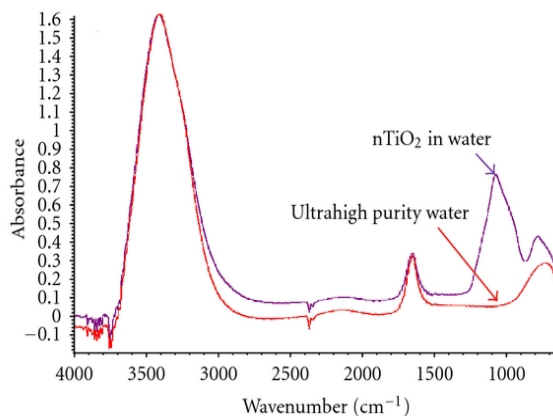


Fig. 1. FT-IR spectra of nTiO₂ colloidal solution in water and of ultra-high purity water.

4. 2. Swelling Measurements

Swelling measurements were carried out by recording the mass of glove material samples after 500 minutes (corresponding to a working day) of immersion in the nTiO₂ solutions during. Fig 2 displays the mass gain recorded for nitrile rubber immersed in the nTiO₂ solution in water. A steady increase is observed. The variation coefficient for the reported data is less than 1%. Swelling measurements were also conducted with the ultra-pure solvents corresponding to the nTiO₂ solution liquid carriers to verify if that mass gain is not caused by an accumulation of nanoparticles in surface features of the samples (Dolez et al. 2010). The curves obtained for the nTiO₂ solution in water and for ultra-high purity water superimpose perfectly as shown in Fig 2. This indicates that the recorded gain mass is solely attributable to the swelling of nitrile rubber by the colloidal solution liquid carrier, water in that case.

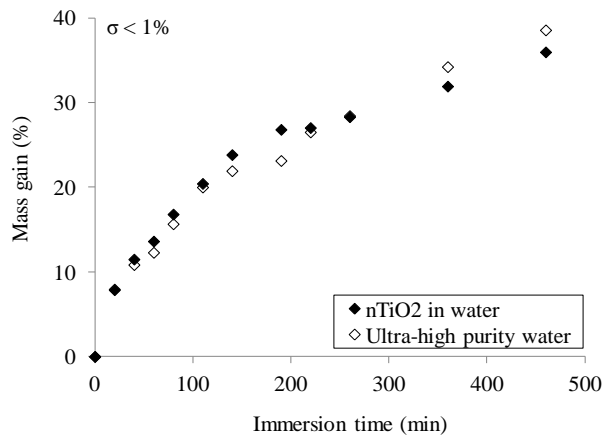


Fig. 2. Variation of mass for nitrile rubber as a function of immersion time in nTiO₂ solution in water and ultra-high purity water.

The measured mass gain for nitrile rubber samples immersed in the three nTiO₂ solutions - in water, EG and PG - as a function of the immersion time is displayed in Fig 3-a. A gradual mass increase is observed for all colloidal solutions. The curves corresponding to nTiO₂ solutions in EG and PG appear to overlap. This indicates a similar affinity of both colloidal solutions with nitrile rubber. It is probably due to the fact that the two liquid carriers belong to the same glycol chemical family. Indeed, solvent chemical family is one of the parameters controlling the swelling ratio of elastomers in solvents (Nohile et al. 2008).

Fig 3-a also shows that the swelling ratio of nitrile rubber in the nTiO₂ solution in water is much higher compared to the two others. After 8 hours of immersion, it reaches a value of 35% for the nTiO₂ solution in water while it is equal to 15% for nTiO₂ in PG and EG. This discrepancy may be attributed to differences in viscosity, molecule size and structure, and polarity between the two solvent families. However, maximum swelling has not been reached for any of the nTiO₂ solutions after 8 hours of immersion time.

In order to fully characterize the swelling behaviour of the four protective glove materials in the nTiO₂ solutions in water, EG and PG, longer immersion times were used. Fig 3-b displays the variation of the mass gain of nitrile rubber, latex, neoprene and butyl rubber samples over 3 days when immersed in the nTiO₂ solution in water. For nitrile rubber, latex and neoprene, a plateau in the swelling curves is observed after about 40 hours of immersion. The variation in mass gain is gradual and starts immediately at the beginning of the immersion in the nTiO₂ solutions. This indicates a diffusion of chemical species in the polymer membrane. In the case of butyl rubber, no significant mass gain was recorded at all. Some differences in the swelling behaviour between nitrile rubber, latex and neoprene can also be observed. Indeed, the maximum mass gain for nitrile rubber has reached about 79% while its value is equal to 27% for latex and 18% for neoprene.

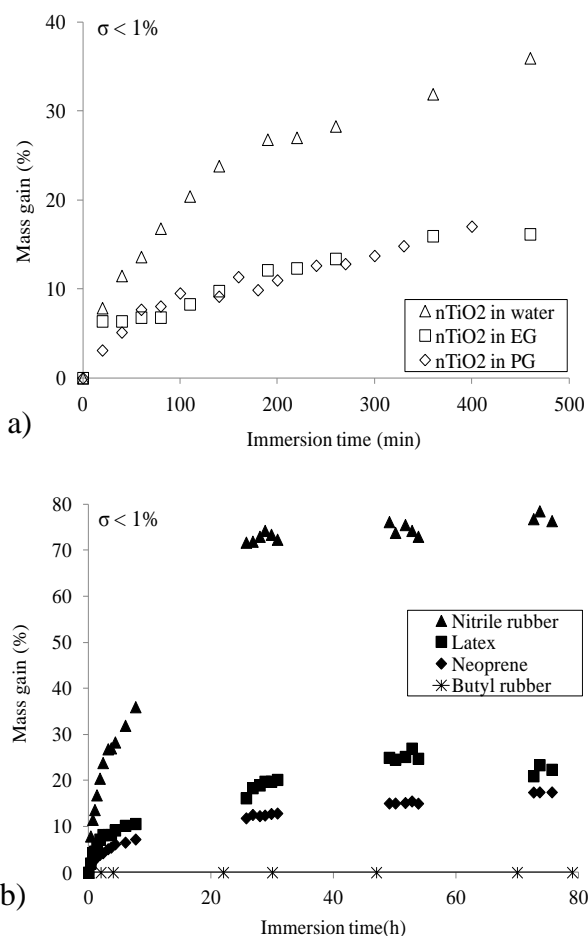


Fig. 3. Variation of mass as a function of immersion time a) in nTiO₂ solution in water, in PG and in EG for nitrile rubber sample and b) in nTiO₂ solution in water for nitrile rubber, neoprene and latex samples.

In Table 1, the maximum mass ratio values measured for the four glove materials and the three nTiO₂ solutions are provided. For each nTiO₂ solutions, the same tendency was observed for the three elastomers. Nitrile rubber swells more than latex which swells more than neoprene. No swelling of butyl rubber was observed in any of the three nTiO₂ solutions.

Using Eq. 5 and the mass gain data, it is possible to estimate the diffusion coefficients of the three nTiO₂ solutions (in water, PG and EG) for nitrile rubber, latex and neoprene. As can be seen in Table 2, the three nTiO₂ liquid carriers diffuse more rapidly in neoprene than in latex and nitrile rubber. It can be attributed to the moderate resistance of neoprene to chemicals (Dolez et al. 2010). It should be noted that nitrile rubber and latex display similar values of diffusion coefficient. In terms of the three nTiO₂ solutions, the nTiO₂ solution in water diffuses faster than the nTiO₂ solution in EG, which diffuses faster than the nTiO₂ solution in PG. It must be noted that these values are quite lower than what

can be measured with more efficient solvents (Perron et al. 2002).

Table 1. Values of maximal swelling ratio for the four glove materials in the three nTiO₂ solutions.

	<i>Maximum mass change ratio (%)</i>		
	nTiO ₂ in water	nTiO ₂ in EG	nTiO ₂ in PG
Nitrile	79	73	94
Latex	27	14	26
Neoprene	18	11	11
Butyl rubber	0	0	0

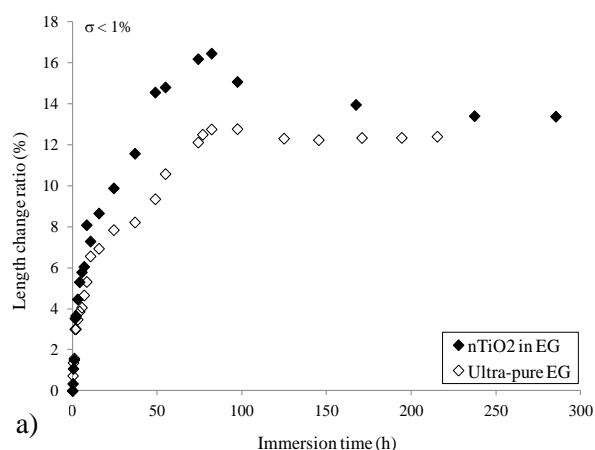
Table 2. Diffusion coefficients of the three nTiO₂ solutions in nitrile rubber, latex and neoprene obtained by mass gain.

	<i>Diffusion coefficients (10⁻¹⁴ m².s⁻¹)</i>		
	nTiO ₂ in water	nTiO ₂ in EG	nTiO ₂ in PG
Nitrile	1.6	0.5	0.7
Latex	1.4	0.4	1.4
Neoprene	10.4	1.5	6.9
Butyl rubber	N/A	N/A	N/A

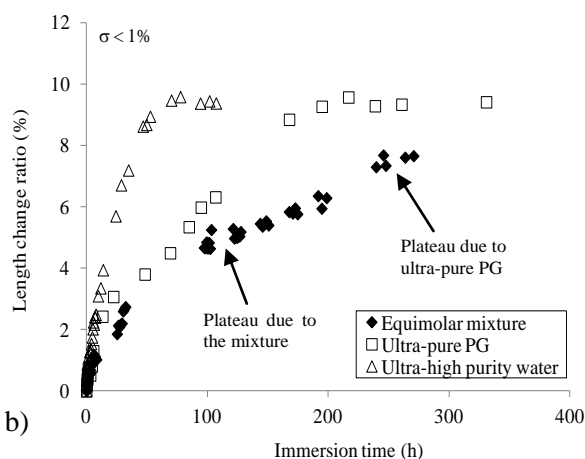
4. 3. Length Change Measurements

The swelling of elastomers in nTiO₂ solutions has also been characterized by measuring the variation in sample length. Fig 4.a displays the results in terms of length change ratio for nitrile rubber immersed in nTiO₂ solution in EG and in ultra-pure EG. The standard deviation for the reported data is less than 1%. A gradual increase in sample length is recorded followed by a plateau. This result confirms the ability of nTiO₂ solution liquid carriers to swell protective glove materials.

Since glycols are known to be highly hygroscopic, measurements were also performed with a mixture of PG and water of known concentration. Fig 4.b compares the variation in time of the length change ratio for nitrile rubber (model 8005-PFL) immersed in an equimolar mixture of ultra pure PG and ultra-high purity water, in ultra-high purity water and in ultra pure PG. In the case of ultra-high purity water and ultra-pure PG, the maxima in length change ratio are both equal to 9.5% but ultra-high purity water seems to diffuse faster than ultra-pure PG. Diffusion coefficient values computed from these data are equal to 2.1×10^{-14} m²/s for ultra-high purity water and 0.8×10^{-14} m²/s for ultra pure PG. For the equimolar mixture, a double plateau can be observed. The first plateau (around 6.5%) may be attributed to the water + PG mixture and the second one (at approximately 8%) could correspond to the diffusion of PG. These results show that great care must be taken during swelling tests to keep hygroscopic solvent-based colloidal anhydrous solutions.



a)



b)

Fig. 4. a) Variation of length change ratio as a function of immersion time in nTiO₂ solution in EG and in ultra-pure EG for nitrile rubber sample and b) Variation in length change ratio as a function of immersion time in a equimolar mixture of ultra pure PG and ultra-high purity water and ultra-high purity water only and ultra-pure PG only for 8005-PFL nitrile rubber samples.

4. 4. Implications for the Protection against Nanoparticles 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 (Fig 5). The swelling of gloves materials, in this case for nitrile rubber, is one of the phenomena which can facilitate the penetration of nTiO₂ solutions through protective gloves (Vinches et al. 2012).

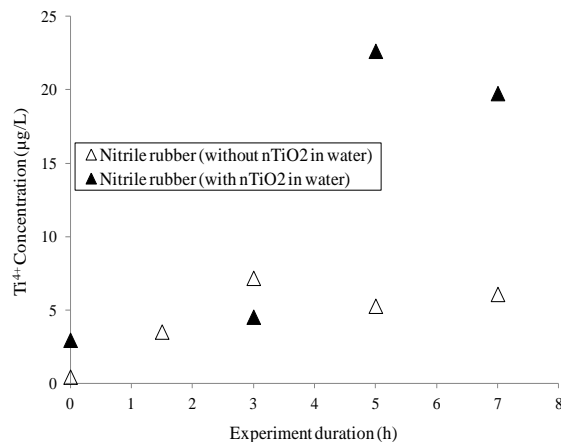


Fig. 5. Variation in titanium concentration in the sampling solutions as a function of test duration for nitrile rubber samples exposed simultaneously to 50% biaxial deformations and nTiO₂ in water.

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5. Conclusion

This paper has investigated the swelling of elastomers used in protective gloves in commercial nanoparticles solutions. Results in terms of mass gain and length change were obtained for four glove materials, nitrile rubber, neoprene, latex and butyl rubber, and three commercial TiO₂ nanoparticles solutions in water, 1,2-ethanediol (EG) and 1,2-propanediol (PG). Tests were also performed with technical and ultra-pure solvents corresponding to the nanoparticle solution liquid carriers. Moreover, complementary analyses FT-IR of the colloidal solutions were also performed.

The studied solutions produce a significant swelling effect on nitrile rubber, latex and neoprene. A large mass gain was recorded for short immersion times (within a few hours), indicating a penetration of the nanoparticle liquid carrier in these elastomers. The highest values of diffusion coefficient were obtained for neoprene, which indicates its larger sensitivity to the three commercial nTiO₂ solutions. On the other hand, no significant swelling of butyl rubber in any of the three colloidal solutions was recorded.

Length change measurements confirm the diffusion of chemical species in nitrile rubber, latex and neoprene samples when immersed in the commercial nanoparticles solutions. They also show a significant action of water mixed with glycols, which indicates that precaution must be taken when conducting swelling measurements in hygroscopic solvents.

These results show that great care must be exercised when selecting protective gloves for handling nanoparticles in solutions. Indeed, as the nanoparticles colloidal solution liquid carrier diffuses through the glove membrane, it may facilitate the transport of the nanoparticles through the protective glove and allow skin exposure. The next step is thus to measure if nanoparticles in solutions can cross protective gloves.

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