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Sean Banaee
Old Dominion University, sbanaee@odu.edu

Shane S. Que Hee

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Original Article

Permeation of ethoxy- and butoxy-ethanols through a disposable nitrile glove

Sean BANAEE[1]* and Shane S. Que HEE[2]

[1]Environmental Health Program, School of Community and Environmental Health, Old Dominion University, USA
[2]Department of Environmental Health Sciences, UCLA Fielding School of Public Health, University of California Los Angeles, USA

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Abstract: The purpose of this study was to investigate the permeation of the glycol ethers, 2-ethoxyethanol (2-EE) and 2-butoxyethanol (2-BE) through disposable, nitrile exam gloves using a modified American Society for Testing and Materials (ASTM) closed-loop module. The purple unsupported, unlined, powderless nitrile glove from Kimberly-Clark was challenged by the two pure glycol ethers. Their permeation parameters were measured with the aid of a 2.54 cm ASTM F739 closed-loop permeation cell using water collection at 35.0 ± 0.5°C in a moving tray water bath, and capillary gas chromatography-mass spectrometry for quantification. Each set of experiments consisted of four standard permeation cells with water as the collection solvent. The steady state permeation rate for 2-EE of 4.83 ± 0.45 µg/cm^2/min was about 4 times that of 2-BE (1.27 ± 0.11 µg/cm^2/min). Permeation of the more nonpolar 2-BE was less than for 2-EE. Both solvents exceeded the ASTM threshold normalized breakthrough time in the closed-loop testing module. Glove samples failed to pass permeation criteria defined by Kimberly Clark and Ansell. Such gloves are not recommended as personal protective equipment for exposure to 2-butoxyethanol or 2-ethoxyethanol, even for very short period exposures. Glove manufacturers should reconsider existing permeation testing method for low volatile compounds and apply the closed-loop module due to higher sensitivity and accuracy.

Key words: Nitrile, Glove, Ethoxyethanol, Butoxyethanol, American Society for Testing and Materials (ASTM), Permeation, Personal protective equipment

Introduction

Protection from dermal exposure to chemicals is necessary to prevent dermatitis and systemic effects after skin absorption[1, 2]. Gloves are the major means of protecting the hands[3]. While much literature is available on chemically protective clothing (CPC) like gloves and their personal protectiveness[4], there is comparatively little information on the protection of chemicals offered by the disposable gloves worn in many non-industrial situations largely because these gloves are not designed to protect against chemicals. Such gloves are preferred to be worn because they facilitate manual manipulation of objects unlike situations that require thicker, heavier CPC gloves[3], and they may be the only ones available in emergencies.

The American Society for Testing and Materials (ASTM) F739-99/12[5, 6] standard defines the permeation process in both closed-loop and open-loop forms[6]. The volatility

*To whom correspondence should be addressed.
E-mail: sbanaee@odu.edu

of the challenge solvent is the major criterion for method selection. Glove manufacturers generally apply the open-loop mode as the default standard method for testing their products while exposed to all volatile and semi-nonvolatile chemicals[7, 8]. In the open loop-module, a carrier gas is constantly flowing across the collection chamber as a dynamic collection medium and captures the vapor of the permeated analyte to a detector. Such model may fit for high volatile compounds to define the breakthrough time and other permeation parameters.

However, with a less volatile chemical, the entire permeated analyte must be evaporated on the collection side and the gas collection system will not be able to define real-time permeation parameters with sufficient accuracy[7, 8]. Therefore, the liquid in the collection system in the closed-loop testing model allows more sensitivity for less volatile compounds. It should also be mentioned that although the liquid collection medium is the key factor for an accurate permeation testing result, a primary study conducted on the solubility of the challenge material in the collection medium is essential[19].

Schwope *et al.*[9] reviewed and compared the open-loop and closed-loop permeation testing models using Fick's law analysis. Although the review indicated no correlation in breakthrough detection time between the two methods, the study only focused on low volatile solvents to compare the above testing models. Klingner *et al.*[10] addressed the lack of standard methods for testing permeation parameters of low volatile compounds with low vapor pressure. Our research group developed the method of immersing the permeation cell in a shaking water bath to simulate gentle force during the permeation process at a specific temperature with simultaneous facilitation of collection and challenge side mixing, with samples taken for analysis from the collection side[11]. Moreover, in the permeation testing model developed by the ASTM and other international standards, room temperature is defined as the default temperature throughout the study[12].

In the current study, two common glycol ethers, 2-butoxyethanol (2-BE; also called ethylene glycol mono n-butyl ether) and 2-ethoxyethanol (2-EE; also called ethylene glycol monoethyl ether) with a wide range of applications in industry were chosen. The glycol ethers are used in toner, ink, paint, varnish, and coatings operations as well as adhesives, sealants, cleaning, degreasing, and many other applications in pharmaceuticals, textiles, and clothing industries[13, 14]. Both are high production chemicals known as solvents with relatively high boiling points of 168°C for 2-BE and 136°C for 2-EE, and both are relatively soluble in water at 25°C[13, 14]. The respective OSHA PEL, NIOSH REL, ACGIH TLV, and NIOSH IDLH values are: 50/200, 5/0.5, 20/5, and 700/500 ppm (v/v), all the 8-h recommendations having a "skin" notation for both. Overexposure to 2-BE primarily causes hematotoxicity and central nervous system effects, while 2-EE is a male and female reproductive toxin[13–15].

All the glove permeation information for these two chemicals is for CPC gloves and the open-loop method with a gas collection carrier. Ansell[8] reported 470 and 293 min detection breakthrough time (DBRT) for Sol-vex nitrile gloves while testing 2-BE and 2-EE respectively (at 0.9–9 μg/cm^2/min permeation rate). Kimberly-Clark Professional[17] cited a >480 min normalized breakthrough time (NBRT) and a 6 μg/cm^2/min steady state permeation rate (SSPR) for G80 nitrile gloves while exposed to 2-BE. The DBRT for 2-butoxyethanol with other gloves was 180 min, 120 min, 45 min, 60 min, and >480 min for unsupported Neoprene, supported Polyvinyl Alcohol, Natural Rubber, Polyvinyl Chloride, and unsupported Viton, respectively[16].

Ansell's permeation studies on 2-BE[8] classifies all unsupported Neoprene, supported Polyvinyl Alcohol, Polyvinyl Chloride, and Natural Rubber as good (G) permeation rate (9–90 μg/cm^2/min) with corresponding breakthrough time as 180 min, 120 min, 60 min, 45 min, and 48 min rate. Forsberg and Keith[4] reported 2-BE NBRTs for nitrile Mapa (Pioneer A-14 and AF-18), Ansell-Edmont (37–155), and North (LA-102G) as >480 min, 420 min, and >420 min, respectively. Ansell reported a 293 min DBRT and 9–90 μg/cm^2/min SSPR for nitrile gloves (Ansell Sol-Vex) exposed to 2-EE.

Kimberly-Clark Professional[17] found >240 min NBRT and 5 μg/cm^2/min SSPR for G80 nitrile gauntlets. The DBRTs for other gloves were 128 min, 75 min, 25 min, 38 min, and 465 min for unsupported Neoprene, supported Polyvinyl Alcohol, Natural Rubber, Polyvinyl Chloride, and unsupported Viton, respectively[8]. Ansell classified SSPR for unsupported Neoprene, supported Polyvinyl Alcohol, and Polyvinyl Chloride in the G (good) category (9–90 μg/cm^2/min), natural Rubber in the VG (very good) category (0.9–9 μg/cm^2/min), and unsupported Viton in the E (excellent) category (<0.9 μg/cm^2/min)[8]. Forsberg and Keith[4] reported 2-EE's DBRT for nitrile Mapa (Pioneer A-14), Ansell-Edmont (37–155), Best (22R), and Magrigold (Blue) as: 416 min, 92 min, 420 min, and 281 min, respectively.

Comparison of all NBRTs/DBRTs for 2-EE and 2-BE reported by Ansell, Kimberly-Clark, and Forsberg shows a shorter NBRT/DBRT and generally larger SSPR for 2-EE for the same glove material. Nitrile appeared to be the most protective apart from Viton, but the latter had no disposable glove counterpart.

Since disposable nitrile gloves are widely used by homeowners and potential exposure while painting, varnishing, or cleaning, a disposable nitrile glove was chosen for the present study. There is no previous study on the permeability of disposable gloves while exposed to 2-EE and 2-BE through the ASTM closed-loop method. This study applies a moving tray water bath and adjusted temperature testing conditions as modifications to the ASTM closed-loop model for permeation of selected glycol ethers and compares the results with the open-loop module.

Materials and Methods

Disposable purple nitrile exam gloves, powder-free, unlined, and unsupported with 24.2 cm length and 0.12 mm thickness from Kimberly-Clark Professional, No. 55082-M were selected. Both analytes, 2-EE and 2-BE with 99% purity, were ordered from Acros Organics.

For the analytical and instrumentational method, gas chromatography mass-spectrometry (GC-MS) was applied with 4-bromophenol (99%) and Helium (99.999%) as the internal standard (IS) and carrier gas respectively. The water used for all aqueous solutions passed through two filtration systems, Millipore Milli-Q Water System and Millipore Ultrapure Water Purification System as a finisher (Temecula, CA, USA).

An Electronic Digital Micrometer Model CO-030025 (0–25 mm, 0.001 mm resolution) from Fisher Scientific was utilized to measure the glove thickness. In order to weigh the glove cuts, a Mettler analytical balance AE260 Scale (Mettler, Hightstown, NJ, USA) was used. A water bath with moving feature was applied to implement the temperature and solvent mixing adjustments as modifications on four ASTM F739-12 permeation cells with 2.54 cm diameter, model I-PTC-600 holding a challenge and collection chamber, aluminum and stainless-steel flanges, Teflon gaskets, and bolts were obtained from Pesce Lab (Kennett Square, PA, USA). More details about the GC–MS system analytical procedures and specifications are published in another report[12].

Procedure

The glove materials were cut from the palm area in two-inch diameter circular pieces and were conditioned in a desiccator at 52 ± 1% and 23°C for 24 h before the permeation test. The experiment was conducted under an atmosphere generated by saturated potassium dichromate at room temperature (23°C). In the next step, the glove cuts' average thickness at marked spots within 1-cm radius of circular area and mass (balance) were defined from triplicate measurements.

The rest of the permeation procedure has been cited in another publication[12]. In summary, 3 permeation cells with 10 ml challenge solvent, 10 ml water collection solvent, and a blank (air challenge with 10 ml water collection solvent) were processed simultaneously using a shaking water bath at 35.0 ± 0.5°C and agitated with a horizontal movement of 7.0 ± 0.5 cm/s which represents a 100 RPM cycle. Aliquots of 0.1 ml were taken from the collection side at 1.0 min, 20 min, 1, 2, 4, 5, 6, and 8 h and deposited into 1.5-ml vials plus 2.0 µl of 0.1 µg/µl internal standard (4-bromophenol). After the permeation test, glove specimens were blotted dry, and reconditioned in the desiccator for thickness and mass measurements.

The linear regression model was used to define the linear relationship features such as slopes, intercepts, standard deviations, standard deviations of the slope and intercept, correlation coefficient (r), and p-values. The independent samples Student t-test was used to determine whether averages were significantly different and to define the p-values of r.

Results and Discussion

The GC-MS linear dynamic range for 2-BE was 0.2 ng to 10.0 ng with 0.2 ng lower quantifiable limit and standardization equation $y=1.3991x-0.123$ with $r^2=0.994$. The retention time for 2-BE and the IS were 4.3 min and 7.5 min, respectively. The run time was 11.00 min. The linear dynamic range for 2-EE was 0.2 ng to 10.0 ng with 0.2 ng lower quantifiable limit and standardization equation $y=7.3611x-0.1314$ with $r^2=0.991$. The retention times for 2-EE and the IS were 7.00 min and 9.50 min, respectively. The run time was 11.92 min.

Table 1 represents the average weight and thickness of the glove specimens before and after permeation.

The average thicknesses for reconditioned glove materials were measured as 107 ± 1 µm and 108 ± 2 µm for 2-BE and 2-EE, respectively. All glove specimens swelled to some extent during the permeation process, but for both 2-BE and 2-EE, it was not more than 10% in any of the samples throughout and after the experiment.

Glove specimens were weighted before and after the experiment. The average weights before and after perme-

Table 1. Average glove thickness (μm) and weight (gr) before and after exposure to 2-EE and 2-BE

Analyte	Thickness before challenging (μm)	Thickness after challenging (μm)	Weight before challenging (mg)	Weight after challenging (mg)
2-EE average	105 ± 2	108 ± 2	299 ± 4	311 ± 10
2-BE average	105 ± 1	107 ± 1	267 ± 6	280 ± 12

2-EE: 2-ethoxyethanol; 2-BE: 2-butoxyethanol.

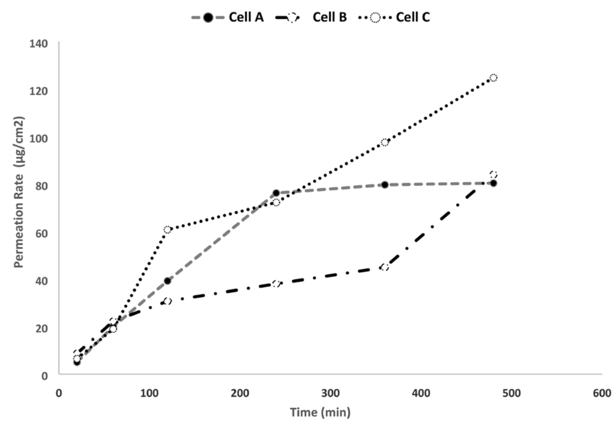

Fig. 1. Permeation of 2-butoxyethanol through purple disposable nitrile gloves.

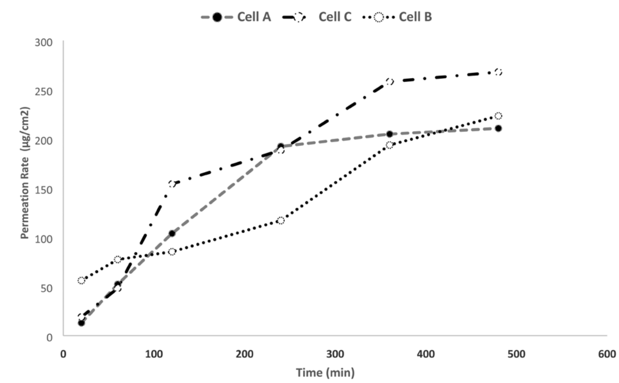

Fig. 2. Permeation of 2-ethoxyethanol through purple disposable nitrile gloves.

ation testing for 2-EE were 0.299 ± 0.004 g and 0.311 ± 0.010 g, respectively. The corresponding weights for 2-BE were 0.267 ± 0.006 g and 0.280 ± 0.012 g. As can be seen, the glove cuts exposed to 2-EE gained an average of 3.2% weight after permeation versus 3.8% for 2-BE. Although all gloves showed some degree of weight appreciation, none of the changes appeared as significant ($p \leq 0.05$).

Since both solvents are known as low volatile with high boiling point, some weight increase is expected as reconditioning may not permit complete evaporation of the solvents inside the glove material. The permeation curves for the 2-BE and 2-EE triplicates are shown in Figs. 1 and 2, respectively. As can be seen, the graph permeation scale for 2-EE is a factor of 50 versus 20 for 2-BE. The SBRT (ASTM 2012) at 0.1 μg/cm^2/min for both solvents was observed within 20 min, with 2-EE being shorter. The trend is consistent with the Ansell study on permeation of 2-EE and 2-BE through Nitrile, Viton Butyl, Neoprene, and polyvinyl alcohol, in which the SBRT for both reported within 30 to 480 min, with an equal or shorter breakthrough time for 2-EE[8)].

Table 2 shows that the average SSPR for 2-BE and 2-EE was 1.27 ± 0.11 μg/cm^2/min and 4.83 ± 0.45 μg/cm^2/min, the latter higher by about a factor of four. The average diffusion coefficient for 2-EE was $(3.8 \pm 1.1) \times 10^{-6}$ cm^2/min, about 2.4 times higher than 2-BE. The 2-EE/2-BE ratio of mass/area permeated after 20 min was 4.4 and at 8 h 2.6. This indicates that 2-EE permeated more than 2-BE. 2-BE is more non-polar and less water soluble than 2-EE because of its longer alkoxy chain. Zellers[18)] conducted a study on modeling the permeation of solvents through CPC Viton glove materials. The study suggests the weighted Hildebrand Solubility Parameter as a simple tool for predicting permeation parameters. Kimberly-Clark[16)] has used NBRT to categorize gloves: <1 min, not recommended; 1–9 min, poor; 10–59 min, good; and 60–480 min as excellent. Such ordering places the tested purple nitrile gloves as “poor” at best.

The permeation studies conducted by the glove manufacturers on disposable nitrile gloves with similar thickness shows a 60–120 min breakthrough time for 2-BE and 30–60 min for 2-EE[20)]. However, the modified closed-loop model shows an earlier breakthrough time and permeation rate for both solvents compared with the values published by the glove manufacturers using the open-loop permeation testing model.

Such observation is supported by multiple factors as the following: a) applying water as collection medium impacted the capability of the closed-loop permeation model in capturing a very small mass of permeated challenge especially for such low volatile analytes, compared with the circulating gas in the open-loop model; b) adjusting

Table 2. Permeation parameters of 2-EE and 2-BE through disposable purple nitrile gloves

Analyte	Replicate	NBRT[a] min	SSPR[b] μg/cm²/min	D[c] × 10^{-6} cm²/min	20-Min Permeated Mass/Area[d]	Total Permeation Mass/Area[e]
2-BE	1	10 ± 10	0.9	1.6	5	80
	2	10 ± 10	1.2	1.3	9	84
	3	10 ± 10	1.4	1.8	6	125
	Average	10 ± 10	1.2 ± 0.25	1.6 ± 0.2	6.6 ± 2.1	96 ± 24
2-EE	1	10 ± 10	3.9	5.6	19	211
	2	10 ± 10	5.1	3.5	26	268
	3	10 ± 10	5.5	2.3	43	262
	Average	10 ± 10	4.8 ± 0.8	3.8 ± 1.2	29 ± 12	247 ± 31

[a]: Normalized breakthrough time; [b]: Steady state permeation rate; [c]: Calculated diffusion coefficient; [d]: μg/cm²; [e]: Permeation rate over 8 h μg/cm².
2-EE: 2-ethoxyethanol; 2-BE: 2-butoxyethanol.

testing temperature based on the real working condition from 21°C to 36°C (15°C increase) shifts permeation parameters through more flexion to the glove texture and provides analyte more freedom to move based on Fick's law permeability. This also simulates real exposure conditions in the workplace; c) the shaking water bath, with optimized RPMs in a horizontal level, created a homogenous distribution of the permeant in the collection chamber. This prevented concentration gradients at the collection side and improved the accuracy of the sampling set as well as breakthrough detection time with detecting permeant at very early stages upon permeation.

Conclusion

Disposable purple nitrile exam gloves showed a higher permeability to 2-thoxyethanol comparing to 2-butoxyethanol. Since the permeation of the analytes exceeded the ASTM threshold normalized breakthrough detection time upon exposure, the gloves were categorized as not recommended with Kimberly-Clark Professional permeation breakthrough time criteria and could not comply with Ansell's triple criteria. The disposable purple nitrile exam gloves should not be used as personal protective equipment for exposure to 2-butoxyethanol or 2-ethoxyethanol even for very short period exposures. Glove manufacturers should reconsider their permeation testing method for low volatile compounds and apply the closed-loop module due to higher sensitivity and accuracy.

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