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Whole glove permeation of cyclohexanol through disposable nitrile gloves on a dextrous robot hand: Fist clenching vs. nonclenching

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Abstract

The differences in permeation parameters when a gloved dextrous robot hand clenched and did not were investigated with the dynamic permeation system described in the companion paper. Increased permeation through the gloves of the present study for cyclohexanol when the gloved hand clenched depended on glove thickness and porosity for cyclohexanol permeation. The Sterling glove, the thinnest and most porous, was the least protective. Hand clenching promoted more permeation for the Sterling glove in terms of breakthrough times, steady state permeation rate, and diffusion coefficient. The Safeskin glove showed increased permeation only for the steady state permeation rate but not breakthrough times or diffusion coefficient. The Blue and Purple gloves showed no differences when the hand was clenching or not. The correlational analysis supported differences between the clenching and non-clenching situations, and the risk assessment considered the worst and best scenarios relative to one and two hydrated hands that were and were not protected by specific gloves.

Keywords

Clenching; cyclohexanol; dextrous robot hand; glove permeation; nitrile gloves

Introduction

The companion article presented the kinetic permeation parameters of cyclohexanol diffusing through nitrile exam gloves worn on an immobile dextrous robot hand with a novel system that allowed sampling of multiple aliquots of circulating collection water containing permeate for subsequent gas chromatography-mass spectrometry (GC-MS) analysis. The results showed that the kinetic parameters collected without clenching of the hand agreed within an order of magnitude or better with the corresponding results of the modified F739 ASTM closed loop technique operated at the same temperature and for the same glove.^[1]

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The next questions answered by this article were if dextrous robot hand clenching relative to the immobile hand would decrease the normalized breakthrough time t_b , the standardized breakthrough time t_s , increase the steady state permeation rate P_s , and increase the diffusion coefficient D. In addition, the influence of such factors as glove thickness, porosity, and acrylonitrile content needed to be determined. The permeation results were then subjected to a risk analysis relative to potential health effects through dermal exposure.

Methods

Gloves, chemicals, robot hand, and procedures

The same gloves and chemicals, robot hand, and procedures were used as in Mathews and Que Hee^[1] except for the conditions used to clench the hand which was set to move every 20 sec to prevent overheating of the relay switch and motor.

Briefly, the Enercell 1.4–12V 300 mA adapter was set to 4.5 V. The adapter was fitted with a 9.0 V snap connector. The relay switch was controlled by a Fisher Scientific Laboratory Timer and Controller using the outlet control. A universal A/C power adapter replaced the 1.5 VDC size AA alkaline battery used originally to power the robotic hand motor. The voltage required to open and close the gloved robotic hand reliably with water running was increased from 1.5 to 3 V DC, the latter being the maximum operating voltage for the motor. The open/close cycle for the robotic hand was optimized to maximize movement force^[2] and minimize heat production from the internal motor. The optimal open/close cycle at 35°C was 20 sec. The clenching force was about 1.8 kg as measured with a Jamar 5030 hydraulic hand dynamometer (Sammons Preston, Bolingbrook, IL). The dynamometer was positioned between the thumb and four fingers. The hand was reliably operational over 8 hr without stopping.

Results

Kinetic and physical parameters

The averaged kinetic data for the whole glove permeation of the clenching and nonclenching dextrous robot hand are presented in Table 1.

The values of t_b and t_s for each glove were not statistically different at p 0.05 for the same clenching condition. Clenching caused statistically different results relative to non-clenching at p 0.05 for the Sterling glove decreasing t_b , t_s , and D, and increasing P_s . Its t_b and t_s on clenching were half those respective parameters for non-clenching. The P_s on clenching was 1.6 times that for non-clenching. The D value on clenching decreased to 57% of the value for non-clenching. All the other comparisons were not significant at p 0.05 except for increased P_s for Safeskin where clenching caused an 18% increase.

The physical parameters for the gloves used for the clenching robot hand are provided in Table 2. The corresponding data for the non-clenching glove are contained in the companion article.^[1]

All thicknesses for the clenching glove increased slightly at p 0.05 after permeation (7.1 to 13.4%, the latter value being for Sterling). The Safeskin, Blue, and Purple gloves basically have the same pre-permeation thickness but the Sterling glove had about 2/3rd the thickness of the other three gloves. The range of pre-permeation thickness values was therefore limited.

Porosity

Porosity relative to pre-permeation decreased after permeation for both clenching and nonclenching for all gloves except for clenching and non-clenching Safeskin; for the nonclenching Sterling glove where there were no statistical differences at p 0.05; and for the clenching Purple glove where porosity was increased (Table 3). Clenching caused less of a decrease than non-clenching with the exception of the Safeskin (no effect) and the clenching Purple glove (increased).

The Safeskin, Blue, and Purple gloves had the same porosity before permeation. The Sterling glove before permeation had about 1.7 fold their porosity. After permeation, only the Blue and Purple gloves showed statistically different porosity relative to non-clenching at p = 0.05 with values about 12% higher than for non-clenching.

The range of pre-permeation porosity values was therefore limited.

Discussion

This is the first reported enhanced permeation effect of simulated fist clenching. The results in Table 1 suggest that clenching the donned dextrous robot hand can increase cyclohexanol permeation through a glove if the latter is thin enough as for the Sterling glove. This is suggestive of a thickness dependence, and increasing thickness should increase t_b and t_s and decrease P_s .

The other kinetic parameter affected by clenching, increased P_s for Safeskin, was unexpected though the effect was small at 18%. However, it did imply that other variables also had to be considered such as acrylonitrile content and porosity.

Glove producers often place higher acrylonitrile content deliberately on the outer challenge surface than on the inside surface^[3] as for the Safeskin, Purple, and Sterling gloves, but the Blue glove was the exception (Table 2). Our research group has published previous work on acrylonitrile content.^[4] Increasing acrylonitrile content may increase t_b and t_s and lower P_s .

Since this is the first report of the porosity property of gloves there are no prior literature data. A more porous glove might be expected to decrease t_b and t_s , and increase P_s . The observed general decrease in porosity after permeation could merely be because not all the high boiling cyclohexanol was removed after permeation and occupied space within the glove membrane or it could be because some inner adsorptive sites were destroyed, questions the current study was not designed to answer.

The results of the companion article^[1] also showed that our modified ASTM F739 closedloop method designed to provide a gentle force on the permeating glove to simulate gentle

hand movement^[5] provided nearly the same simple kinetic parameter results as the nonclenching robot hand for all parameters except for Safeskin (longer t_b and t_s and smaller P_s and D), Blue (bigger P_s), Purple (lower t_s), and Sterling (shorter t_b , longer t_s , and longer P_s), all being ascribed there to their thickness differences for the ASTM experiments. Thus, the results of the comparison between the clenching and non-clenching hand are probably the same for the comparison between the clenching hand and the modified ASTM closed loop data.

There were no statistical differences between t_s and t_b for the whole glove experiments whether clenching or non-clenching. When t_s was regressed with t_b , only the clenching hand was correlated to t_b with r = 0.9860 at p = 0.05 for a null hypothesis of no association where r is the correlation coefficient of the linear regression. The lack of statistical significance for the non-moving hand may be because of small numbers causing lack of statistical power.

Correlations among permeation parameters with thickness (L), outer surface acrylonitrile content (A), pre-permeation porosity (P_o), and permeation area (Q)

When each kinetic parameter (P_s , t_b , t_s , D) was regressed linearly one-on-one with the independent variables (L,A,P_o,Q), the following were statistically significant at r = [0.9750] at p = 0.05 assuming the Student *t* distribution for a sample number n = 4 and 2 degrees of freedom: P_s vs. L with r = -0.9794 for ASTM F793; t_b vs. L with r = 0.9910; t_s vs. L with r = 0.9793; t_s vs. P_o with r = -0.9968 for the non-clenching robot hand; and P_s vs. L with r = -0.9820 for the clenching robot hand. A and Q were not involved in any one-on-one correlations, probably because they did not differ enough for each glove exposure situation and because of low sample number. It has already been indicated above that the Sterling glove has very different L, A, and P_o from the other gloves. While Q is a constant for the ASTM F739 Method at 5.06 cm² its absolute value differs a lot from those of the whole glove experiments. Q is nearly constant for the whole glove experiments—the average exposed area of 1141 ± 73 cm² having a coefficient of variation of 4.7% (Table 2). The manner in which the whole glove experiments were done ensured that Q was not a factor similar to temperature, and preconditioning.

There was no common correlation that was statistically significant for all three situations but P_s vs. L showed a significant negative correlation for ASTM F739 and the clenching robot hand. The non-clenching *r* was -0.9377, near the p = 0.05 threshold *r* of -0.9750.

These screening results reinforced the idea that the permeation parameters might require multivariate relationships among the independent variables to optimize r and hence p in spite of the limited range of values for each parameter.

The above one-on-one results for t_b and t_s for the non-clenching hand suggest a relationship of the type $t_i \ a \ L^x A^y / (P_o^z Q)$ for each glove exposure situation where x,y,z are exponents that vary between 0–4 for $t_i = t_b$ or t_s and for D.

The inverse relationships might be expected for P_s . An iterative process to optimize the independent variables and their exponents relative to *r* and hence *p* was then initiated.

For the modified ASTM F739 method, the following were statistically significant at r = 0.9750 for p = 0.05:

$$P_{s}$$
 vs. L^{2}/P_{o}^{2} , vs. L^{2}/P_{o}^{3} , vs. L^{3}/P_{o}^{2} , vs. L^{3}/P_{o}^{3} , vs. L^{4}/P_{o}^{3} , vs. L^{3}/P_{o}^{4} , and vs. L^{4}/P_{o}^{4} ,

all r having negative values.

The highest *r* was for P_S vs. L^3/P_0^3 with r = -0.9898 (eqn. 1) as compared with P_s vs. L with r = -0.9794 (eqn. 2). The two regression equations were:

$$P_{\rm s} = -2.29 \times 10^{5} (L^{3} / P_{\rm o}^{-3}) + 21.7 \tag{1}$$

$$P_{\rm s} = -394\,\mathrm{L} + 52.3\tag{2}$$

The addition of the second independent variable did help improve the simplistic analysis but L still provides the bulk of the correlation. Similar to the non-clenching hand, the following were statistically significant at r = |0.9750| for p = 0.05:

$$t_s vs. L/P_0$$
, $vs. L^2/P_0$, and L/P_0^2 ,

all *r* having positive values.

The correlation with the highest r was t_s vs. L^2/P_o with r = 0.9958 (3) as compared with t_s vs. L where r = 0.9793 (4) and with t_s vs. P_o where r = -0.9968 (5):

$$t_{\rm s} = 1761 (L^2/P_{\rm o}) + 9.72 \tag{3}$$

$$t_{\rm s} = 168L - 1.36\tag{4}$$

$$t_s = -3.66P_0 + 30.8$$
 (5)

Both independent variables are important because they oppose each other's effects.

Similarly for the clenching hand, the following were statistically significant at r |0.9750| for p = 0.05:

$$t_s$$
 vs. L/P₀, and vs. L²/P₀²,

with all *r* having positive values.

$$P_{s}$$
 vs. L/P_{o} , vs. L^{2}/Q , vs. L^{2}/P_{o}^{2} , vs. L^{2}/QP_{o}^{2} vs. L^{3}/P_{o}^{2} , vs. L^{3}/QP_{o}^{2} , vs. L^{2}/P_{o}^{3} , vs. L^{2}/QP_{o}^{3} , vs. L^{3}/QP_{o}^{4} , vs. L^{2}/P_{o} , vs. L^{2}/QP_{o}^{3} ,

For t_s , the highest *r* was vs. L/P₀ where r = 0.9794 (6). There was no correlation with L, L/Q, P₀, or P₀/Q:

$$t_s = 445(L/P_0) - 1.12 \tag{6}$$

For P_s, the highest *r* was vs. L/P₀ where r = -0.9951 (7) compared with r = -0.9820 for vs. L (8):

$$P_{\rm s} = -706(L/P_{\rm o}) + 40.4\tag{7}$$

$$P_{\rm s} = -376 \,\mathrm{L} + 59.2 \tag{8}$$

The inclusion of P_0 improved the correlation.

The correlations differ for the unclenching and clenching hand indicative of an effect of clenching although both had correlations for t_s . The unclenching hand had no correlations for P_s . The clenching hand had similar correlations for P_s observed for the modified ASTM F739 method but had different optima relative to *r*. No correlations contained A for *p* 0.05, probably because of the small range of A values and low sample numbers.

These correlations need to be confirmed with other chemicals, with the new Lavender nitrile glove that is thinner than the Sterling glove, and with a robot hand that has a more forceful clench force than the current 1.8 kg since thinner materials will be most sensitive to a high clench force.

Risk assessment

An estimation of health risk to a glove wearer is an important applied aspect of glove permeation data.

Cyclohexanol has a American Conference of Governmental Industrial Hygienists threshold limit value TLV over 8 hr of 50 ppm,^[6] the same value as the National Institute for Occupational Safety and Health recommended exposure limit, and the Occupational Safety and Health Administration's permissible exposure limit.^[7] The guidelines are based on eye irritation and central nervous system impairment. The latter, being a systemic effect, will also be elicited by absorption of cyclohexanol through the skin. There are no specific short term exposure limits (STEL). If excursion guidelines are assumed,^[6] an approximate STEL over 30 min would be 150 ppm with a ceiling of 250 ppm, with the TLV not exceeded.

The latter provides an exposure situation that corresponds to Kimberly-Clark disposable glove classifications for t_b :^[8] <1 min, not recommended; 1–9 min, poor; 10–59 min, good;

and 60–480 min, excellent. This is so because disposable gloves are usually doffed at breaks, after a maximum exposure duration of 2 hr.

If 150 ppm (615 mg/m³) of cyclohexanol is inhaled for 30 min, the maximum dose in mg absorbed assuming all was absorbed would be this concentration multiplied by the volume breathed in over 30 min at moderate work. If 10 m³ is the volume breathed in over an 8-hr day at moderate physical activity, then in 30 min the volume breathed in is $(30/480) \times 10 \text{ m}^3 = 0.625 \text{ m}^3$. This volume at an air concentration of 150 ppm over 30 min would contain 384 mg of cyclohexanol.

If there was no inhalation exposure, and the only exposure route was skin absorption then the threshold skin absorbed dose is 384 mg at the end of 30 min of skin exposure. The rate of cyclohexanol permeating the skin can be calculated from the Revised Robinson model of skin absorption.^[9]

The maximum flux through the skin J_{max} in mg/cm²/h is provided by (9):

$$U_{\max} = KS, \tag{9}$$

where K is the permeation coefficient in cm/h and S the water solubility of the chemical in mg/cm^3 for hydrated skin, that is, skin that has protective layers of water, the usual exposure situation.

Equation (9) does not predict exposure to dry skin by pure chemical or if the chemical dehydrates the skin surface since partition coefficients including water are assumed in (10) and (11).

K is a complex factor that reflects the resistance of the stratum corneum (the skin outer layer) in its lipid (K_L), protein (K_P), and water (K_W) compartments by their dependencies on the octanol-water coefficient (K_{ow}) and molecular weight (MW) of the chemical via (10)–(13):

$$K = 1/[1/(K_{\rm L} + K_{\rm P}) + 1/K_{\rm W}]$$
(10)

$$\log K_{\rm L} = -1.326 + 0.6097 \log K_{\rm ow} - 0.1786 \,\rm{MW}^{0.5}$$
(11)

$$K_{\rm P} = 0.0001519/MW^{0.5} \tag{12}$$

$$K_W = 2.5/MW^{0.5}$$
 (13)

Cyclohexanol has the following specific values:^[10] MW = 100.16; log K_{ow} = 1.23; S = 43 mg/cm³ and substitution into (10)–(13) yields:

$$\begin{split} \kappa_L &= 0.004335 \text{ cm/h}, K_P = 0.000015 \text{ cm/h}; \text{ and} \\ \kappa_W &= 0.2498 \text{ cm}, /h, K = 0.00428, \text{ and} \\ J_{max} &= 0.184 \text{mg/ cm}^2/h \,. \end{split}$$

The amount absorbed depends on the time of exposure (0.5 hr) and the area exposed. If the hands and wrists are exposed, this constitutes an exposed area of 2000 cm² for a reference man of 70 kg.^[11] Thus, the dose absorbed or cumulated mass absorbed is $0.184 \times 2000 \times 0.5 = 184$ mg or 48% of the 30-min excursion threshold dose of 384 mg, nearly half the allowable dose. If the area of exposure is taken to be the mean glove exposed area of 1141 cm² for one hand exposure (a very common scenario), the exposure is $0.184 \times 1141 \times 0.5 = 105$ mg. or 27% of the excursion threshold.

For the situation of nitrile disposable glove protection, since t_b is defined as the time when the glove permeation is 250 ng/cm²,^[12] this would constitute a potential breakthrough mass exposure of 0.5 mg, well below the 30-min mass threshold of 384 mg for cyclohexanol.

A worst-case scenario occurs at the steady state permeation period for the clenching Sterling glove. The P_s was 29 μ g/cm²/min. This is equivalent to 0.029 \times 2000 \times 30 = 1,740 mg, well above the 30-min excursion dose threshold. At the steady state rate, the critical time to reach 384 mg is 0.029 \times 2000 \times t = 384 mg or 6.62 min. For one hand, the permeated mass is 0.029 \times 1141 \times 30 = 993 mg and the critical time is 11.6 min.

Since the Sterling glove $t_b = t_s$ for the clenching glove, the glove permeation rate was about 100 ng/cm²/min.^[13] In terms of the skin absorption units of cyclohexanol, this permeation rate is equivalent to $0.0001 \times 60 = 0.006$ mg/cm²/h, some 31 times lower than the absorption rate of cyclohexanol through skin. The P_s is equivalent to 1.74 mg/cm²/h, much higher than the skin absorption rate of 0.184 mg/cm²/h. Thus, the skin will become occluded, will become wet, and may allow more skin permeation than predicted by (9).

The Safeskin and Blue gloves were the most protective with breakthrough times of about 20 min and P_s of about 10 µg/cm²/min. The latter rate is about one third that of the Sterling glove when clenching. Thus, the critical times to meet the excursion threshold will be about three times that of the Sterling glove, that is, about 20 min for 2 hands, and about 35 min for one.

The potential mass to expose the skin when glove permeation occurs depends on the shape of the permeated mass/time vs. time curve after breakthrough. It can be calculated directly from the area under the curve. Usually, the permeation rate vs. time curve shape is not linear until the steady state, although two linear periods have been measured by our group in other glove-chemical systems. The actual mass to expose the skin depends also on the tightness of fit of the glove, the degree of hand flexing, and the degree of perspiration that allows hydration of the skin. Using the potential exposure mass is a useful worst case scenario for hydrated skin.

Risk assessment for skin irritation is still largely empirical. Cyclohexanol is classified as a mild-to-moderate skin irritant based on skin Draize *in vivo* tests and human keratinocyte *in vitro* data.^[14] Its irritancy effects tend to be delayed and not immediate.

The best practice when wearing disposable gloves of unknown permeation performance is to double-glove.

Conclusions

Hand clenching promoted more cyclohexanol permeation only for the Sterling glove in terms of breakthrough times, steady state permeation rate, and diffusion coefficient. Increased permeation through all the gloves when the gloved hand clenched depended on glove thickness and porosity. The Sterling glove, the thinnest and the most porous, was the least protective. The Safeskin glove showed increased permeation on clenching only for the steady state permeation rate but not breakthrough times or diffusion coefficient. The Blue and Purple gloves showed no differences when the hand was clenching or not. The correlational analysis supported differences between the clenching and non-clenching situations, and the risk assessment considered the worst and best scenarios relative to one and two hands with hydrated skin that were and were not protected by gloves.

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Glove	Breakthrough time t_b/t_s^a (min)	Steady state permeation rate [°] (µg/cm ² /min)	Diffusion coefficient (cm ² /min) $\times 10^{-5}$
Safeskin			
Whole Glove (NC) $n = 3$	$20 \pm 3/20 \pm 4$	$10.0\pm0.7,$ good	60 ± 20
Whole Glove (C) $n = 3$	$14 \pm 4/16 \pm 4$	$11.8\pm0.7,\mathrm{good}^{d}$	68 ± 15
Blue			
Whole Glove (NC) $n = 4$	$22\pm5/20\pm4$	9 ± 1 , very good	35 ± 13
Whole Glove (C) $n = 3$	$18\pm5/20\pm4$	7 ± 1 , very good	44 ± 23
Purple			
Whole Glove (NC) $n = 3$	$18\pm0/20\pm4$	14 ± 3 , good	46 ± 11
Whole Glove (C) $n = 3$	$18\pm0/18\pm0$	11.4 ± 0.6 , good	47 ± 9
Sterling			
Whole Glove (NC) $n = 3$	$12\pm0/12\pm0$	18 ± 2 good	35 ± 5
Whole Glove (C) n = 3	$6\pm 0^{d}/6\pm 0^{d}$	$29 \pm 3 \mod^d$	20 ± 3^d

c Apparent because of slight swelling (<10%) during the experiment but no statistical difference relative to original thickness at p 0.05 on reconditioning.

 $d_{\rm Statistically}$ different at p 0.05 relative to the non-clenching whole glove.

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Glove	Acrylonitrile % outside n = 20	Acrylonitrile % inside n = 20	Glove area (cm ²) n = 3	Thickness pre-permeation (mm) $n = 30$	Thickness post-permeation (mm) n = 30
Safeskin	13 ± 2^{a}	9.8 ± 0.5^{a}	1125 ± 9	0.13 ± 0.01	$0.14\pm0.01^{{b}}$
Blue	12 ± 1	12 ± 1	1242 ± 10	0.14 ± 0.01	$0.15\pm0.01b$
Purple	17.2 ± 0.7	12.1 ± 0.7^{a}	1129 ± 51	0.12 ± 0.01	$0.13\pm0.01b$
Sterling	17.1 ± 0.8	12 ± 1^{a}	1067 ± 10	0.082 ± 0.010	$0.093\pm0.010^{{\color{black}}b}$

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 $^{\prime\prime}$ Statistically different at p 0.05 relative to pre-permeation.

Table 3.

Glove Porosity for clenching (C) and non-clenching (NC) whole gloves before and after permeation.

Glove	Porosity pre-permeation (m ² /g)	Porosity post-permeation NC/C (m ² /g)
Safeskin (n = 3)	2.83 ± 0.09	$3.00 \pm 0.40/2.91 \pm 0.09$
Blue (n = 3)	3.04 ± 0.07	$2.57 \pm 0.04^{a}/2.88 \pm 0.07^{a,b}$
Purple (n = 3)	2.97 ± 0.04	$2.83 \pm 0.05^{a} / 3.18 \pm 0.09^{a,b}$
Sterling (n = 3)	5.12 ± 0.03	$4.50 \pm 0.50 / 4.79 \pm 0.07^{a}$

 a Post-permeation statistically different at p 0.05 relative to pre-permeation.

 b C is statistically different from NC at p 0.05.