

Assessment of skin exposure to N,N-dimethylformamide and methyl ethylketone through
chemical protective gloves and decontamination of gloves for reuse purposes

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ABSTRACT

N,N-dimethylformamide (DMF) and methyl ethylketone (MEK) are the hazardous chemicals commonly used in the synthetic leather industries. Although chemical protective gloves provide adequate skin exposure protection to workers in these industries, there is currently no clear guideline or understanding with regard to the use duration of these gloves. In this study, the permeation of DMF/MEK mixture through neoprene gloves and the desorption of chemicals from contaminated gloves were conducted using the ASTM F739 cell. The acceptable use duration time of the gloves against DMF/MEK permeation was estimated by assuming a critical body burden of chemical exposure as a result of dermal absorption. In a re-exposure cycle of 5 days, decontamination of the gloves by aeration at 25°C was found to be inadequate in a reduction of breakthrough time as compared to a new unexposed glove. However, decontamination of the gloves by heating at 70 or 100°C showed that the protective coefficient of the exposed gloves had similar levels of resistance to DMF/MEK as that of new gloves. Implications of this study include an understanding of the use duration of neoprene gloves and proper decontamination of chemical protective gloves for reuse.

Keywords: synthetic leather industry; ASTM F739; dermal absorption; protective coefficient.

1. Introduction

N,N-dimethylformamide (DMF) and methyl ethylketone (MEK) are widely used as solvents in the dry manufacturing processes of synthetic leather industries. Several studies have indicated that dermal absorption is an important route for human DMF exposures (Wang et al., 2007; Mraz and Nohova, 1992). DMF and MEK are of the acute toxicity and assigned a skin notation (RTECS[®], 2001). They may cause skin irritation, abdominal pain, and nausea. For the workers who handle DMF and MEK routinely on the job, chemical protective gloves provide a mechanism to protect them against the skin exposure of the hazardous materials. However, researches in the past have shown that chemical protective gloves are not indefinitely impervious to organic solvents which may permeate through the gloves at a molecular level (Chao et al., 2006; Perkins, 2003). Except for disposal gloves, the chemical protective gloves are usually reused in practice. Once the gloves are contaminated, the resistance of the gloves to the chemical may be degraded, resulting in faster breakthrough of the chemicals in the reused gloves compared to the permeation through the new gloves, consequently increasing the risk of exposure to the chemicals (Ziskin et al., 2003; Klingner and Boeniger, 2002; Zellers et al., 1992). Therefore, it is critical to assess the effective decontamination methods of chemical protective gloves for reuse.

Methods of decontamination for chemical protective gloves should not pose any hazards to the users or the environment (Ziskin et al., 2003). In general, the chemicals may be removed from the gloves by means of surface-wipe, rinse, evaporation, or thermal desorption (Gao et al., 2005; Zellers et al., 1992; Vahdat and Delaney, 1989). Rinsing contaminated protective gloves with surfactants or organic solvents can be effective. However, the use of surfactants and solvents is not cost-effective and may risk damaging the gloves (Gao et al., 2005). Vahdat and Delaney (1989) indicated that washing gloves with detergents along with

aeration did not effectively remove organic solvents from neoprene, nitrile, and butyl gloves.

Laboratory tests such as ASTM F739 and ISO 6529 using permeation cells are frequently performed to evaluate the resistance of chemical protective gloves against chemical permeation (Henry and Stull, 2003). These methods typically determine the profile of concentration of the chemicals in the collection medium over time after it permeates through the gloves. Once a concentration profile is established, the breakthrough time and the permeation rate of the chemical in the gloves can be determined, and used to evaluate the resistance of the gloves (Perkins, 2003; Henry and Stull, 2003).

Chemicals of skin exposure hazards such as DMF are conventionally assigned a skin notation by a regulatory agency or occupational management organization to recognize their capacity in contributing significantly towards the overall exposure and potential of systemic toxicity by route of skin absorption (Boeniger and Ahlers, 2003). However, at this time quantitative limits of skin exposure for these skin exposure hazards are not established (Boeniger and Klingner, 2002). This matter is further exacerbated in that there are chemicals known to be significantly absorbed via the skin but currently not assigned a skin notation. To better inform the workers about the health hazards from skin exposure to these chemicals and the protective equipments to consider, there is a need to estimate the acceptable duration for the use of specific types of protective gloves against the permeation of hazardous chemicals.

In this study, the permeation of DMF/MEK mixture through neoprene gloves was conducted using the ASTM F739 cell. After the permeation experiments, desorption of DMF and MEK from the contaminated gloves in the clean collection medium was investigated. Based on the acute toxicity of DMF and MEK, modeling was performed to evaluate the acceptable duration for wear of neoprene gloves. In addition, the efficacy of decontaminated neoprene gloves protecting against DMF/MEK permeation was examined where the contaminated glove samples

were thermally decontaminated, and then re-exposed to the DMF/MEK mixture for a cycle of four times, simulating a practical scenario of glove reuse. The decontamination efficiency of the re-exposed gloves was evaluated based on the permeability coefficients and standardized breakthrough times of the decontaminated gloves. The study described herein provides an understanding on the effectiveness of chemical protective gloves in reuse to protect against harmful exposure to hazardous chemicals.

2. Materials and methods

2.1 Glove samples and chemicals

Test specimens were cut from the palm portion of neoprene gloves (MAPA 414319, Brunswick, OH), rinsed with de-ionized water, and air-dried for 24 h at a temperature of $25\pm 1^\circ\text{C}$ and relative humidity of $50\pm 5\%$. The thicknesses of glove samples were measured at five random locations to the nearest 0.01 mm using a dial thickness gauge (Teclock Co., Okaya, Japan). The average thickness of the glove samples was 0.75 ± 0.03 mm. DMF (Mallinckrodt, Paris, KY), MEK (Riedel-deHaën, Seelze, Germany) and methanol (Mallinckrodt, Phillipsburg, NJ) were all of GC grade with purity greater than 99%.

2.2 Permeation of DMF/MEK through gloves

The permeation test of DMF/MEK mixture ($v=1:1$) was conducted using the ASTM F739 method (2007) with a closed-loop system. The schematic flow diagram of the experimental apparatus is shown in Fig. 1. The stainless steel permeation cell (Pesce Lab Sales, Kennett Square, PA) with a diameter of 25-mm was separated by the glove sample into the collection and challenge chambers. Depending on the nature of test chemical, the collection medium flowing through the test cell can be distilled water or solvents. However, an appropriate collection

medium is used not to simulate the characteristics of human body, e.g. sweat (Henry and Stull, 2003). The solvent collection medium, such as Hexane and 2-propanol (IPA), has been conducted for the permeant with the low water solubility (Phalen and Que Hee, 2003; Xu and Que Hee, 2007). Because of the low solubility of DMF in water, methanol was used as the collection medium in this study. It was noted that the back permeation of methanol through neoprene gloves should be investigated prior to conducting the permeation test of DMF/MEK mixture.

In the closed-loop system, methanol was circulated through the collection chamber using a MasterFlex[®] PTFE-Tubing pump system (Cole-Parmer, Vernon Hills, IL) at a flow rate of 100 mL/min. The total volume of collection medium was 170 mL. As shown in Fig. 1, a spherical stirrer was used to mix the collection medium in the Teflon bottle. All equipment constituting the closed-loop system was connected with Teflon tubing (Cole-Parmer, Vernon Hills, IL) and placed in an incubator at a temperature of $25\pm 1^{\circ}\text{C}$.

During the permeation test, one- μL aliquots of methanol were collected from the downstream sampling point using a micro-syringe every 15 min. The samples were directly injected into a gas chromatograph with flame ionization detector (GC/FID, Auto-System XL, Perkin Elmer, Norwalk, CT). The temperature of the GC capillary column (EquityTM-1, Supelco, Bellefonte, PA) was increased from 40 to 180°C at a rate of $20^{\circ}\text{C}/\text{min}$. The temperatures of the injection port and detector were maintained at 200 and 250°C , respectively. Limit detection levels (LDLs) of GC/FID for DMF and MEK in methanol were 0.34 and 1.12 mg/L, respectively. The permeation test was conducted until a constant rate of permeation occurred, which indicated that the permeation of DMF/MEK mixture through neoprene had reached a steady state.

2.3 Back permeation of methanol through neoprene

Back permeation of the collection medium through glove samples could soften the sample and reduce the permeation resistance of challenge chemical. In this study, the back permeation of methanol through neoprene gloves was investigated using an open-loop system for ASTM F739 (Chao et al., 2007). As shown in Fig. 2, the permeation cell was immersed in a water bath at a temperature of $25\pm 1^\circ\text{C}$. Nitrogen gas used as the collection medium was supplied by a cylinder with a flow rate of 200 ± 10 mL/min. During the back permeation experiments, 50 μL gaseous samples were taken using a gas-tight syringe from the downstream sampling point every 10 min intervals. The gaseous samples were immediately injected into the GC/FID. LDL for methanol in nitrogen gas was 0.18 mg/L. From the open-loop test, methanol did not permeate through neoprene samples during the 4 h study. Therefore, methanol is an appropriate collection medium for the DMF/MEK mixture.

2.4 Desorption of DMF/MEK from gloves

The permeation test as described in Section 2.2 was terminated when DMF and MEK concentrations in the collection medium were increased linearly, i.e. reaching steady state permeation. The permeation cell was immediately disassembled. The test specimen was blotted dry to remove excess liquid chemicals using filter papers, and then placed in a second permeation cell. With the test glove sample in place, the closed-loop system of the second cell was reassembled using fresh methanol circulating through the collection chamber, and the elapsed time for the desorption experiment was clocked.

The challenge chamber of the second permeation cell was emptied of chemical, simulating the case where a worker wears the used gloves but without additional contact with the chemical. Reassembling of the second cell was usually completed within 10 min, and the experimental

apparatuses were subsequently placed back in an incubator at $25\pm 1^{\circ}\text{C}$. The sampling procedure was similar to that previously described in Section 2.2. As DMF and MEK in methanol reached constant concentrations, the desorption experiments were terminated and the DMF/MEK concentrations appearing in the emptied challenge chamber were analyzed using GC/FID.

2.5 Glove resistance altered by decontamination and in reuse

To evaluate the reusability of decontaminated neoprene gloves to protect against DMF and MEK, the glove samples were first contaminated with the chemical, decontaminated, and then re-exposed to the chemical. The change in the chemical's breakthrough time and steady state permeation rate through the glove sample was observed and compared to determine the change in the glove's resistance to the chemical. In the decontamination study, the task was conducted for 5 d in succession to simulate the use of protective gloves and the challenge of chemical exposure in a working week. After the first permeation test of a cycle, the specimen was decontaminated and then re-exposed to the DMF/MEK mixture following the permeation test, which was repeated successively for four times in a cycle.

Two procedures of decontamination, i.e. rinse and thermal treatment, were attempted. In the first decontamination method, the contaminated samples were rinsed using 20 mL deionized water within 1 min and then air-dried at $25\pm 1^{\circ}\text{C}$ overnight. This decontamination procedure is comparable to those commonly practiced in industries. In the thermal decontamination method, the contaminated samples were heated in an oven at temperatures of 40, 70 and 100°C for 2 or 10 h, respectively. The thermally treated glove samples were then aerated at $25\pm 1^{\circ}\text{C}$ overnight before re-challenged by DMF/MEK. The thermal decontamination procedures were selected as researches have reported that no degradation of the neoprene material was visually detected even when heated for 16 h at 100°C (Gao and Tomasovic, 2005; Vahdat and Delaney, 1989).

3. Results and discussion

3.1 Permeation of DMF/MEK mixture

Fig. 3 shows the permeation results for the DMF/MEK mixture. Once breakthrough has occurred, the DMF and MEK concentrations in the collection medium were found to increase linearly. For a closed-loop system, the steady state permeation rate, J_s ($\text{ML}^{-2}\text{T}^{-1}$), was calculated by plotting the permeant concentrations versus time as follows:

$$J_s = \alpha_p \frac{V}{A} \quad (1)$$

where α_p is the slope of linear portion, i.e. steady state permeation, of the DMF/MEK concentrations in the collection medium ($\text{ML}^{-3}\text{T}^{-1}$); V is the total volume of the collection medium in the closed-loop system (L^3); and A is the area of glove sample exposed to the permeant, i.e., 5.06 cm^2 .

During the permeation test, the total volume of the samples withdrawn from the collection medium was less than $15 \mu\text{L}$. Therefore, the total volume of the collection medium was assumed to be constant in the closed-loop system. The steady state permeation rate is known to be inversely proportional to the thickness, L (L), of glove samples. To account for the effect of sample thickness, the resistance of neoprene sample was quantified using the permeability coefficient, P ($\text{ML}^{-1}\text{T}^{-1}$), as follows (Chao et al., 2007):

$$P = J_s L \quad (2)$$

ASTM F739 specifies the standardized breakthrough time (*SBT*) at which the permeation rate of $0.1 \mu\text{g}/\text{cm}^2/\text{min}$ is detected (ASTM F739, 2007). For the closed-loop system, the standardized breakthrough time is principally dependent on the frequency of the permeant sampling and sensitivity of the analytical instrument. During the permeation experiment of this study, the collection medium was sampled every 15 min interval. Therefore, the minimum

sensitivities of the GC/FID should be as low as 0.045 mg/L to detect a permeation rate of 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$. Several standard methods for the permeation test specify the breakthrough time at which the permeation rate reaches the detection limit (ISO 6529, 2001; EN 374-3, 2003). Due to the sensitivity of GC/FID for DMF and MEK, *SBT* of this study was determined based on the elapsed time when the permeation rate reached 10 $\mu\text{g}/\text{cm}^2/\text{min}$.

Table 1 presents the permeability coefficients and standardized breakthrough time of DMF/MEK mixture in the neoprene gloves. *SBT* for DMF and MEK was 45.1 ± 1.2 and 34.3 ± 0.7 min, respectively. Also shown in Table 1, the permeability coefficients were 21.9 ± 1.8 and 23.6 ± 2.1 $\mu\text{g}/\text{cm}/\text{min}$ for DMF and MEK, respectively. With a higher *P* and a shorter *SBT*, MEK is more permeable through the neoprene gloves than DMF.

One-dimensional diffusion of chemical into the glove membrane can be expressed by Fick's second law as follows:

$$\frac{\partial C_z}{\partial t} = D \frac{\partial^2 C_z}{\partial Z^2} \quad (3)$$

where *D* is the diffusion coefficient of the permeant in the glove membrane (L^2T^{-1}); C_z is the permeant concentration at some point *Z* in the glove membrane (ML^{-3}); and *Z* is the distance along the direction of diffusion (*L*).

In this study, the boundary and initial conditions of Eq. (3) were assumed as:

$$\begin{aligned} C_z(0, t) &= S_p \\ C_z(L, t) &= 0 \\ C_z(Z, 0) &= 0 \end{aligned}$$

where S_p is the solubility of the permeant in the glove membrane (ML^{-3}).

By solving Eq. (3), the concentration profile C_z into the glove membrane was given as follows:

$$C_z(Z,t) = S_p \left(1 - \frac{Z}{L}\right) - \sum_{n=1}^{\infty} \frac{2S_p}{n\pi} \exp\left(-D \left(\frac{n\pi}{L}\right)^2 t\right) \sin\left(n\pi \frac{Z}{L}\right) \quad (4)$$

For the steady state, i.e., $t \rightarrow \infty$, the concentration profile C_Z was described as follows:

$$C_z(Z,t) = S_p \left(1 - \frac{Z}{L}\right) \quad (5)$$

By taking the mass balance for the collection medium, the concentration of permeant, C (ML^{-3}), in the closed-loop system was determined as follows:

$$V \frac{dC}{dt} = -AD \frac{\partial C_Z}{\partial Z} \Big|_{Z=L} = -AD f(t) \quad (6)$$

where $f(t) = \frac{\partial C_Z}{\partial Z} \Big|_{Z=L}$. C can be solved from Eq. (6) as follows:

$$C = -\frac{AD}{V} \int f(t) dt + C^* \quad (7)$$

With the initial condition of $C(0)=0$, the integration constant C^* can be determined.

According to the solutions of Eq. (4), the diffusion coefficient and solubility may be experimentally obtained by (Crank, 1975; Chao et al., 2007):

$$D = \frac{L^2}{6 t_l} \quad (8)$$

$$S_p = \frac{P}{D} \quad (9)$$

where t_l is the lag time (T) which is given by the extrapolation of the steady state portion of the permeation curve to the time axis.

As shown in Table 1, the diffusion coefficients for DMF and MEK were 1.39 ± 0.14 and 1.69 ± 0.23 ($10^{-5} \text{ cm}^2/\text{min}$), respectively, indicating that MEK permeated faster through the neoprene sample than DMF. Also shown in Table 1, S_p estimated using Eq. (9) was 1.7 ± 0.17 and 1.26 ± 0.21 (10^6 mg/L) for DMF and MEK, respectively. The permeation concentration with

respect to time in Eq. (7) was solved using the Maple software (Waterloo Maple Inc., Waterloo, Ontario, Canada). Fig. 3 shows the results of simulation using Eq. (7) and its comparison to the observations from the permeation experiments for DMF/MEK mixture. It can be seen that the diffusion coefficient estimated from Eq. (8) was able to approximately simulate the permeation results with S_p as the boundary condition.

3.2 Duration of safe use of neoprene gloves against DMF/MEK permeation

Dermal exposure of DMF and MEK may occur immediately once they permeate through the neoprene glove. The permeated chemical accumulates in the space between the glove and the skin surface, thus resembling a closed microenvironment. DMF carries a skin notation and has been shown to permeate rapidly through the skin. The permeation rate of DMF through the human skin is $156 \mu\text{g}/\text{cm}^2/\text{min}$ (Mraz and Nohova, 1992), whereas in this study an average steady state permeation rate of $279.2 \mu\text{g}/\text{cm}^2/\text{min}$ was observed for DMF through neoprene gloves. A factor of dermal absorption of the glove permeant, defined as the ratio of the skin permeation rate to the glove permeation rate, F_d , could be determined for DMF, and was found to be approximately 60%. An exposed skin area, A_s , of 410 cm^2 was assumed for one hand (Boeniger and Klingner, 2002). If a worker of 70 kg wore a neoprene glove and was continuously exposed to DMF for the duration of T_u , the level of DMF body burden resulting from the acute skin absorption of DMF through one hand, i.e. Dermal Dose, might be estimated as follows:

$$\text{Dermal Dose} = J_s \times F_d \times A_s \times T_u \times \frac{1}{70 \text{ kg}} \quad (10)$$

The dermal lethal dose 50% (LD_{50}) of DMF, representing the acute dermal toxicity, for rabbits was $4,720 \text{ mg}/\text{kg}$ (RTECS®, 2001). An uncertainty factor (UF) of 10 was applied to compensate for the uncertainty inherent in the animal-to-human extrapolation of dose-response

relationship (LaGrega et al., 1994). As this information was applied in the Dermal Dose model, DMF was found to pose a potential health risk to the worker who came into contact with DMF for longer than 481 min, excluding the time prior to the establishment of the steady state permeation.

$$\begin{aligned} \text{Dermal Dose} &= LD_{50} \times \frac{1}{UF} \quad (11) \\ \Rightarrow 279.2 \mu\text{g}/\text{cm}^2/\text{min} \times 0.6 \times 410 \text{ cm}^2 \times T_u \times \frac{1}{70 \text{ kg}} &= 4,720 \text{ mg}/\text{kg} \times \frac{1}{10} \\ \Rightarrow T_u &= 481 \text{ min} \end{aligned}$$

For MEK, the permeation rate through the human skin was $10.5 \mu\text{g}/\text{cm}^2/\text{min}$ (Wilschut et al., 1995), and the average steady state permeation rate through the neoprene glove found in this study was $321.3 \mu\text{g}/\text{cm}^2/\text{min}$. Subsequently, F_{da} in the case of MEK was 3.3%. The dermal LD_{50} of MEK for rabbits was 6,480 mg/kg (RTECS[®], 2001). As calculated using Eq. (11), the duration of acceptable exposure of one hand to MEK was found to be 10,434 min.

$$\begin{aligned} 321.3 \mu\text{g}/\text{cm}^2/\text{min} \times 0.033 \times 410 \text{ cm}^2 \times T_u \times \frac{1}{70 \text{ kg}} &= 6,480 \text{ mg}/\text{kg} \times \frac{1}{10} \\ \Rightarrow T_u &= 10,434 \text{ min} \end{aligned}$$

In compliance with the T_u determined for DMF, the lower of the two values estimated for DMF and MEK in the event of skin exposure to individual chemical, the workers wearing the test glove should not be continuously exposed to the mixture of DMF/MEK for more than 481 min, assuming there were no toxicological interactions between DMF and MEK. The steady state permeation rate for MEK was higher than that of DMF, but based on T_u the risk of dermal absorption was mainly attributed to DMF. Because of the co-solvent effect, the assessment of the risk from the skin absorption of DMF/MEK mixture should be conducted, if desired, using the results of permeation test for the mixture of these solvents in a formulation as actually applied in the manufacturing process (Chao et al., 2008; Purdham et al., 2001). If the worker was

exposed to DMF/MEK via both the routes of inhalation and dermal absorption simultaneously, T_u should be less than the values calculated herein.

Boeniger and Klingner (2002) estimated the acceptable wear duration of protective gloves using the airborne Occupational Exposure Limit (OEL). In their study, the exposure of workers via the inhalation route was calculated using an 8-h respiratory volume of 10 m^3 and an airborne concentration of 50% OEL (i.e., the action level). Furthermore, they assumed the skin exposure limit, SL , was equal to half of the chemical dose the worker absorbed in the body through inhalation when exposed to the chemical in the air at a concentration of 50% OEL. The 8-hour time-weighted average of the OSHA PEL or ACGIH TLV[®] (RTECS[®], 2001) for DMF was 30 mg/m^3 . The skin exposure limit of DMF could be derived as:

$$SL = \frac{1}{2} \text{Inhalation Dose} \quad (12)$$

$$\Rightarrow SL = \frac{1}{2} (10 \text{ m}^3 \times 0.5 \text{ OEL}) = \frac{1}{2} (10 \text{ m}^3 \times 0.5 \times 30 \text{ mg/m}^3) = 75 \text{ mg}$$

The absorbed rate, R_a , of DMF by the gloved hand was calculated as follows:

$$R_a = J_s \times F_d \times A_s = 279.2 \text{ } \mu\text{g/cm}^2/\text{min} \times 0.6 \times 410 \text{ cm}^2 = 68.68 \text{ mg/min}$$

For a worker wearing the test glove, the allowable time for skin exposure to DMF was then determined to be (Boeniger and Klingner, 2002):

$$\frac{SL}{R_a} = \frac{75 \text{ mg}}{68.68 \text{ mg/min}} = 1.1 \text{ min}$$

Based on the OEL model described earlier, the allowable time for skin exposure to DMF was much less than the estimate projected by the Dermal Dose model. The variation as observed herein might be attributed to the very difference in the reference selected in these two models to indicate the level of acceptable body burden, i.e. LD₅₀ and OEL. Derived from a dose-response relationship, the dermal LD₅₀ is the median dose of a toxic chemical that when

applied on the animal skin may be absorbed through the skin and subsequently result in the death of half the test animals.

In comparison, the OEL value is often set to prevent the occurrence of any adverse effects from inhalation exposure, and is frequently derived by applying additional uncertainty factors to the lowest observed human/animal intoxication level. As a result, when the same health endpoint was compared, the OEL could be more protective than the LD₅₀, resulting in a lower T_u projected by the OEL model than the level by the Dermal Dose model. In addition, the OEL mainly concerns the chemical absorbed via the lungs during inhalation exposure, and at times may focus on different health effects than those considered the most sensitive when the skin is a target organ. Nonetheless, our evaluation herein suggests that the evaluation for the permeation rate of chemical through human skin should be a pre-requisite to the assessment of the health risk associated with using protective gloves. For practical purposes, it should be noted that the material characteristics, such as swelling, stretching, and abrasion, may have an effect on the duration of safe use of protective gloves.

3.3 Concentration profile of residual DMF/MEK

Fig. 4 shows the desorption concentrations of DMF/MEK in methanol collection medium. Even without contacting the permeant, the residual DMF/MEK was desorbed from the contaminated glove samples. As seen in Fig. 4, the DMF/MEK concentrations were significantly increased in the collection medium and then remained constant at, approximately, a level of 210 and 189 mg/ L for DMF and MEK, respectively. The volume of the collection methanol was 170 mL, and the residual DMF and MEK desorbed from the gloves was approximately 35.7 and 32.1 mg, respectively, during a test period of 260 min. These findings

suggest that desorption of DMF and MEK may occur and pose a threat to the worker if the gloves are contaminated and reused before proper decontamination.

At the end of the desorption experiment, DMF and MEK volatilized into the emptied challenge chamber were less than 1 and 5%, respectively, of the desorbed mass. These amounts were minute and could be neglected for the modeling purposes. In the desorption experiment, the initial residual concentrations of DMF/MEK inside the contaminated glove were assumed to follow a linear concentration gradient profile as described by Eq. (5). For the desorption experiment, the boundary and initial conditions of Eq. (3) were assumed to be:

$$\begin{aligned} C_z(0, t) &= 0 \\ C_z(L, t) &= 0 \\ C_z(Z, 0) &= S_d \left(1 - \frac{Z}{L} \right) \end{aligned}$$

where S_d was the solubility of the permeant in the contaminated glove (ML^{-3}).

The concentration profile of DMF/MEK inside the contaminated glove was then calculated using Eq. (3) to give:

$$C_z(Z, t) = \sum_{n=1}^{\infty} \frac{2S_d}{n\pi} \exp \left(-D \left(\frac{n\pi}{L} \right)^2 t \right) \sin \left(n\pi \frac{Z}{L} \right) \quad (13)$$

By substituting Eq. (13) into Eq. (6), the concentration of DMF/MEK in the collection medium can be determined with an initial condition of $C(0)=0$. For the desorption experiments, the diffusion coefficients of DMF and MEK were assumed to be the same as that of the permeation experiments given in Table 1. The solubility S_d was determined using the sum of the least squares method. By minimizing the sum of the squares of the deviations of the measured concentrations from the values predicted by the proposed model, a critical value of S_d for Eq. (14) giving the best approximation can be obtained by solving:

$$\frac{d}{dS_d} \left(\sum_i (C(t_i; S_d) - C_{d,i})^2 \right) = 0 \quad (14)$$

where $C_{d,i}$ is the measured concentration at a specific time t_i .

Fig. 4 presents the curve fitting results which can appropriately match DMF and MEK concentrations in the collection medium during desorption experiments. Fig. 5 shows that the curve fitting results were significantly correlated ($R^2=0.9821$, $p<0.05$) to the experimental concentrations in the collection medium. Also seen in Fig. 5, the results were very close to 1:1 line, indicating an excellent agreement between the experimental and modeling results. As shown in Table 1, the values of S_d for DMF and MEK were 0.58 ± 0.09 and 0.52 ± 0.08 (10^6 mg/L), respectively, which were lower than those obtained from the permeation experiments, i.e. S_p . One plausible explanation for this observation was that DMF/MEK in glove samples was desorbed from their surface during the reassembling process in the desorption experiments. This phenomenon was consistent with the conditions for practical glove use in the workplace. Nonetheless, Eq. (13) provides an approach to describe the concentration profile of the residual permeant inside a contaminated glove, which will be a model to assess the health risk of wearing the used glove for workers.

3.4 Resistance of decontaminated gloves to chemical permeation

Table 2 shows the normalized permeability coefficients (P_i/P_1) and standardized breakthrough times (SBT_i/SBT_1) for the DMF/MEK mixture in the decontamination and re-exposure study. When the decontamination was conducted at 25°C, the average normalized $SBTs$ were 0.69 ± 0.23 and 0.62 ± 0.21 min for DMF and MEK, respectively. As indicated in Fig. 6, the breakthrough times of the third to fifth re-exposure were significantly shorter than that of

the new glove sample. This might be resulted from the ineffective decontamination conducted at 25°C. The residual DMF/MEK, i.e. not removed from the glove sample, permeated first through the re-exposed glove, which shortened the breakthrough times for the DMF/MEK mixture.

Fig. 7 shows that the permeability coefficients of DMF and MEK at 25°C as obtained from the re-exposure tests were also less than those of the new samples for DMF and MEK. This observation suggests that the steady state permeation rates of DMF/MEK through the re-exposed samples were decreased compared to the rates through the new samples. One possible reason is the effect of dissolution of additives, such as plasticizers, from the neoprene gloves during the permeation tests (Gao and Tomasovic, 2005). The plasticizers may weaken the interaction between the neoprene molecules, thus enhancing the free movement of DMF/MEK. As DMF/MEK dissolved the plasticizer in neoprene samples, the properties of the re-exposed samples in resisting chemical permeation were also altered from those of the new ones. Therefore, the permeability of DMF/MEK through the re-exposed samples was reduced. Similar results were found in the re-exposed samples decontaminated at 40, 70, and 100°C.

As presented in Table 2, the average normalized *SBTs* of DMF/MEK for the re-exposed samples, decontaminated at 40 and 70°C, were lower than those for their new ones. It was speculated that the residual DMF/MEK was not sufficiently decontaminated from the glove samples at these temperatures. DMF and MEK might be thermally desorbed when the glove samples were treated at 100°C for over 2 h, but the plasticizers might be also leached out from the glove samples. As a result, DMF and MEK permeated slowly through the glove samples.

In order to compare the effectiveness of decontamination methods, the ratio of average normalized permeability coefficient to standardized breakthrough time, defined as protective coefficient, was determined as follows:

$$P_c = \frac{\overline{NP}}{\overline{NT}} = \frac{\overline{(P_i/P_1)}}{\overline{(BT_i/BT_1)}} \quad (15)$$

An increase in permeability or a decrease in breakthrough time will adversely affect the permeation resistance of chemical protective gloves. Thus, a decontamination method is deemed effective when P_c is less than one. Fig. 8 compares the protective coefficients of DMF and MEK for the glove samples decontaminated using different methods. Aeration at 25°C appears to be the worst decontamination method, because its corresponding protective coefficient for DMF was the highest, i.e. 1.3, among all attempted methods. Decontamination at 40°C for either 2 or 10 h was not effective to recover the resistance of neoprene gloves to DMF permeation. On the other hand, P_c was the lowest for DMF and MEK for the re-exposed gloves thermally decontaminated at 100°C for 10 h. In this study, heating at 70 or 100°C appears to be the appropriate decontamination method.

After re-exposure for 4 times, the microstructures of neoprene samples were examined using scanning electron microscope (SEM, JSM-5400, JEOL, Japan) to secure high resolution images of glove surfaces. Fig. 9 shows that the decontaminated neoprene samples were noticeably different in morphology from the new samples. The dark image of neoprene surface was increased with the temperatures used in the decontamination method, suggesting that the material properties of the neoprene samples might not be the same at different temperatures of decontamination. This variation may be attributed to an additional cross-linking of the neoprene polymers during the thermal decontamination process or the dissolution of plasticizers from neoprene samples. Therefore, the test of physical properties, such as tear resistance, should be conducted to ensure the decontaminated gloves are not degraded before these gloves are adequate to be reused (Gao and Tomasovic, 2005).

4. Conclusions

For a mixture of DMF and MEK evaluated in this study, MEK had a higher permeability coefficient and a shorter breakthrough time as compared to that of DMF, rendering MEK of these two chemicals more permeable through the neoprene gloves. Even without continuous contact with the DMF/MEK mixture, desorption of residual DMF and MEK from the contaminated glove occurred. Based on Fick's law, the concentrations of DMF and MEK in the collection medium for the permeation and desorption experiments were appropriately predicted.

The risk of dermal absorption of the mixture was mainly attributed to DMF, since the rate of DMF permeating through human skin was significantly higher than that of MEK. According to the acute dermal toxicity of DMF and MEK, the acceptable wear duration of test gloves was 481 min. As compared with the OEL model, the Dermal Dose model developed herein can be an appropriate method to estimate the duration of safe use of protective gloves against chemicals. It should be noted that the permeation resistance to the DMF/MEK mixture should be determined using the chemical constituents in their actual composition as applied in industrial processes.

Based on the assessment of the protective coefficients, decontamination of neoprene gloves at 70 or 100°C resulted in the recovery of the permeation resistance of gloves to DMF/MEK to levels similar to those found in new gloves. The chemical resistance of neoprene gloves to DMF was the worst when the gloves were decontaminated at 25°C. Further studies are needed to investigate the effect of plasticizers on the chemical resistance of protective gloves during the process of decontamination.

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