

Permeation of Hair Dye Ingredients, *p*-Phenylenediamine and Aminophenol Isomers, through Protective Gloves

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Skin irritation and contact allergies are skin disorders common to hairdressers. The predominant oxidative hair dye components, such as *p*-phenylenediamine (PPD) and aminophenol isomers, can cause contact dermatitis. Use of protective gloves can prevent dermal contact with skin irritants. This study investigates the permeation behaviors of *p*-aminophenol (PAP), *m*-aminophenol (MAP), *o*-aminophenol (OAP) and PPD in single and mixed challenge solutions with disposable natural rubber latex (NRL) gloves, disposable polyvinylchloride (PVC) gloves and neoprene (NP) gloves. The challenge solutions were 4% PPD (w/v), 3% OAP (w/v), 2% PAP (w/v) and 2% MAP (w/v) in ethanol or 12% hydrogen peroxide solutions. The cocktail solutions of the four chemicals were also tested. An American Society for Testing and Materials type permeation cell, ethanol liquid collection and gas chromatography–flame ionization detection of samples taken from the collection medium every 10 min facilitated determination of breakthrough times (BTs), cumulative permeated masses and steady-state permeation rates (SSPRs). Experiments were 4 h long for the NRL and PVC gloves and 8 h for NP gloves. No chemicals tested broke through the NP gloves when exposed for 8 h. In the ethanol solution, PPD and OAP started breaking through the PVC gloves at 40 min. The SSPRs of PVC gloves were higher than those for NRL gloves in all challenge conditions for both single chemicals and mixtures. No tested chemicals in hydrogen peroxide solutions permeated the gloves during the 4-h tests. The chemical composition of the challenge solution was a main effector of BTs and SSPRs for the NRL glove. For disposable PVC gloves, the main factors of BTs were molecular size [molar volume (MV)] and polarity ($\log K_{ow}$), and the primary factors of SSPRs were concentration, MV and $\log K_{ow}$. In conclusion, disposable NRL gloves and disposable PVC gloves should not be used repeatedly for handling the hair dye products. Hydrogen peroxide did not accelerate chemical breakthrough. The compositions of the challenge solutions and physical and chemical properties (MV and $\log K_{ow}$) affected permeation behaviors for different gloves.

Keywords: aminophenols; chemical-protective gloves; hair dyes; permeation; *p*-phenylenediamine

INTRODUCTION

The International Agency of Research on Cancer (IARC) estimated that the number of hairdressers and barbers worldwide in 1993 totaled several millions. Approximately, 35% of women and 10% of men in Europe, Japan and the USA have used hair colorants (IARC, 1993). Notably, hairdressers have an increased risk of occupational skin diseases due to exposure to skin irritants and sensitizers (Uter

et al., 2003). Hair dyes are categorized by the coloring persistence, permanent hair dyes (oxidative hair dyes), semipermanent hair dyes and temporary hair dyes (IARC, 1993). Oxidative hair dyes contain primary intermediates and couplers. The primary intermediates are *p*-phenylenediamine (PPD), *o*-aminophenol (OAP), *p*-aminophenol (PAP) or *p*-toluenediamine, whereas the couplers are *m*-aminophenol (MAP), *m*-hydroxyphenol or resorcinol. When mixing intermediates and couplers, the primary intermediates initially react with hydrogen peroxide to form a diimine, and the diimine then reacts with couplers to form dinuclear, trinuclear or polynuclear structures. The small molecules (unreacted primary intermediates and couplers) diffuse into hair,

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start coupling reactions and then become trapped in hair (Nohynek *et al.*, 2004; Rastogi *et al.*, 2001; Bolt and Golka, 2007). A skin exposure assessment study indicated that hairdressers were exposed to compounds in permanent hair dyes during dye application and when cutting newly dyed hair (Lind *et al.*, 2005). Thus, the unreacted chemicals entrapped in hair increased the probabilities of contacting these chemicals.

Several epidemiological studies reported that occupational exposure to hair dyes caused an increased risk of bladder cancer for male hairdressers (IARC, 1993; Czene *et al.*, 2003; Kogevinas *et al.*, 2003; Gaertner *et al.*, 2004). Those who have worked as hairdressers or barbers for at least 10 years have a 5-fold increase in risk compared with individuals not exposed to hair dyes (Gago-Dominguez *et al.*, 2001). Several recent meta-analyses of epidemiological studies concluded that insignificant causal association exists between a hair dye user and bladder cancer (Hunchareik and Kupelnick, 2005; Takkouche *et al.*, 2005; Kogevinas *et al.*, 2006; Lin *et al.*, 2006; Kelsh *et al.*, 2008).

Hairdressers typically come in contact with different hair products, such as hair dyes, during work (Iorizzo *et al.*, 2002; S¸stet *et al.*, 2004, 2005). The sites of hair dye contact allergies for hairdressers are hands and forearms (Iorizzo *et al.*, 2002; S¸stet *et al.*, 2002). A German study demonstrated that 73.1% of all hairdressers experienced occupational contact dermatitis, 89.3% of which had contact dermatitis on the hands (Uter *et al.*, 2003). Uter's group also reported a high prevalence of hairdressers' contact allergies to PPD according to the data from Information Network of Departments of Dermatology (Uter *et al.*, 2007).

Several studies have identified PPD and aminophenol isomers, which are the major components of commercial oxidative hair dye products (especially in Taiwan), as common allergens for hair dye (Wu *et al.*, 1997). Varying degrees of chronic inflammation of the skin were observed in mice after contact with the oxidative hair dyes for a period of 20 months (Jacobs *et al.*, 1984). Notably, PPD is one of the most potent contact allergens. Of the 29% of the persons who had adverse reactions to hair dyes and underwent patch tests, all were positive for allergic reaction to PPD (S¸stet *et al.*, 2002). Wearing appropriate protective gloves while contacting the hair dyes to limit the exposure to allergic chemicals for hairdressers is recommended (Nixon *et al.*, 2006). Nitrile rubber gloves have been tested for 5% PPD (w/v) and no breakthrough was detected at 4 h (Lind *et al.*, 2007).

Permeation occurs when a chemical contacts the glove surface and diffuses through the glove material. The chemical molecules traveling through the glove material then contact skin. Several factors affect the ability of a given chemical to permeate through glove materials. The important factors are the glove material itself, additives used during glove manufacturing, the manufacturing process and glove

material thickness. Permeation parameters primarily include breakthrough time (BT) and steady-state permeation rate (SSPR). These parameters indicate how long gloves provide reliable protection when contacting a particular chemical. These parameters are also critical references for selection and use of gloves. Therefore, evaluating the permeation parameters of chemical-protective clothing in contact with different chemicals is necessary.

The aims of this study were as follows: (i) determine the permeation parameters of PPD, PAP, MAP and OAP while challenging disposable natural rubber latex (NRL) gloves, disposable polyvinylchloride (PVC) gloves and neoprene (NP), gloves using the American Society for Testing and Materials (ASTM) F739 method, (ii) investigate the effect of hydrogen peroxide on hair dye permeation, (iii) recommend the appropriate protective gloves to wear when dealing with hair dye products and (iv) determine which factors affect the permeation behavior for these investigated gloves.

MATERIALS AND METHODS

Gloves and chemicals

Three gloves were subjected to permeation tests: disposable powder-free NRL gloves (DERMA-GRIP®, D1501-30, WRP Asia Pacific Sdn Bhd, Sepeng, Malaysia), disposable PVC gloves (9" PVC gloves, P0014-9, Carry Hi Technical Corporation, Taipei County, Taiwan) and NP gloves (Neoprene™, 29-865, Ansell, Red Bank, NJ, USA). The disposable NRL gloves and disposable PVC gloves are available at affordable prices and used widely by hairdressers. The NP gloves have good permeation resistance against ethanol and hydrogen peroxide solution according to the manufacturer's test data.

Four hair dye ingredients were selected based on an up-to-date literature review and survey of common commercial hair dye products in Taiwan (Wu *et al.*, 1997). The PPD (CAS: 106-50-3, GC/NT grade, purity $\geq 97.0\%$), PAP (CAS: 123-30-8, grade, purity $\geq 97\%$) and MAP (CAS: 519-27-5, technical grade, purity $\geq 98\%$) were from Fluka (Steinheim, Germany) and OAP (CAS: 95-55-6, technical grade, purity 99%) was obtained from Aldrich, Munich, Germany. The internal standard, biphenyl (CAS: 92-52-4, GC grade, purity 98%) was also acquired from Fluka. Ethanol (CAS: 64-17-5, purity 95%) was purchased from Taiwan Sugar Corporation (Tainan, Taiwan). The 35% hydrogen peroxide solution (CAS: 7722-84-1) was obtained from Riedel-de Haën (Hanover, Germany).

Apparatus

The ASTM-type I-PTC-600 permeation test cells were obtained from Pesce Lab Sales (Kennett

Square, PA, USA). A micrometer screw gauge (SM-112 00-398-04, Teclock, Tokyo, Japan) was used to measure glove thickness at seven random points before and after each permeation experiment. A torque wrench (OP-60, Onpin, Taichung, Taiwan) ensured equal tightness of permeation cell nuts. An analytical electrical balance (XS 204, Mettler Toledo, Greifensee, Switzerland) was employed to weigh the glove samples before and after each permeation experiment.

Chemical analysis utilized an Agilent 7890A gas chromatograph with 7683B autoinjector module and flame ionization detector (GC-FID) (Santa Clara, CA, USA). The fused capillary column was a Restek Rtx®-35 30 m × 0.25 mm I.D. with 0.25- μ m film (Bellefonte, PA, USA). The carrier gas, nitrogen, was 99.999% pure and had a flow rate of 0.8 ml min⁻¹ (Shengyi Gas, Taipei, Taiwan).

Methods

The permeation test was a modified closed-loop system of the ASTM F739-07 method (ASTM, 2007) and has been described elsewhere (Lin and Que Hee 1998a,b,c). In summary, the glove materials from the palm or back parts of the gloves were cut into circles (diameter = 5 cm). The specimens were conditioned for 24 h in a desiccator at 21.6 ± 1.6% relative humidity at room temperature before permeation tests. The glove sample was held between the two Teflon gaskets of the permeation cell. Two glass chambers were inserted into the aluminum flanges, and the nuts were tightened using a torque wrench. The exposed area of the glove material was 4.2 cm². A volume of 15 ml ethanol was added as the collection medium and 15 ml of challenge solution was pipetted into the challenge chamber. Different challenge solutions were tested (Table 1). The concentrations of each test chemicals were decided according to the legislatively allowable maximum concentrations of Council of the European Communities, Taiwan Department of Health and US Food and Drug Administration. Ethanol was used as the dilution solution because of the solubilities of the four investigated chemicals. Hydrogen peroxide was a solvent to mix hair dye cream before application. It was used to simulate the real hair dye application situation in

this study. Aliquots of 990 μ l were taken at 10-min intervals from the collection side and then introduced into 1.5-ml brown vials. A 1- μ l aliquot of the permeation sample was injected into the GC-FID via the autoinjector module. The same volume (990 μ l) of fresh ethanol was replenished into the collection side immediately after each sampling to maintain the total volume of the collection medium at 15 ml during the entire permeation experiment. A discontinuous shaking was performed every 10 min, i.e. before taking the samples and after replenishing the collection medium. Experiment durations were 4 h for disposable gloves (NRL and PVC) and 8 h for the NP gloves. At the end of each permeation experiment, the permeation cell was disassembled to remove the glove sample. The glove specimen was then weighed and its thickness measured immediately after being patted dry using a Kimwipe. Permeation tests were performed at a thermostatic-controlled room with average temperature of 21 ± 1°C. All experiments were performed in triplicate.

Operating conditions for GC-FID were as follows: 280°C for the injector, 250°C for the detector; initial column temperature was 60°C for 2 min, increasing to 150°C at 15°C min⁻¹, held for 5 min and then increased to 280°C at 35°C min⁻¹ and then held for additional 2 min. The nitrogen carrier gas flow rate was 0.8 ml min⁻¹. All chemicals including internal standard eluted within 15 min (Fig. 1). Internal standard calibration curves were generated for each analysis day. The GC-FID linear ranges of the analytical method were 1–10 ng μ l⁻¹ for OAP, 1.5–10 ng μ l⁻¹ for PAP and PPD and 2–10 ng μ l⁻¹ for MAP. The minimum detectable mass permeated for the four chemicals in the collection solution were 15 μ g for OAP, 22.5 μ g for PAP and PPD and 30 μ g for MAP.

The BT was the elapsed time between initial application of a chemical in the exposure compartment and its subsequent presence on the other side of the material (ASTM, 2007). Theoretically, SSPP is determined when the increase in permeation becomes constant relative to time. The total permeated mass of each chemical in the collection medium was calculated from the mass in the 1- μ l injection using the internal standard method corrected for the fraction injected and for the mass in the previous permeation samples. Cumulative permeated mass was

Table 1. The compositions of the challenge solutions

Chemicals	PPD	PAP	MAP	OAP
Ethanol solution				
Single chemical (w/v%)	4% (40 mg ml ⁻¹)	2% (20 mg ml ⁻¹)	2% (20 mg ml ⁻¹)	3% (30 mg ml ⁻¹)
Mixtures ^a (w/v%)	1% (10 mg ml ⁻¹)	0.75% (7.5 mg ml ⁻¹)	0.5% (5.0 mg ml ⁻¹)	0.75% (7.5 mg ml ⁻¹)
12% Hydrogen peroxide solution				
Single chemical (w/v%)	4% (40 mg ml ⁻¹)	2% (20 mg ml ⁻¹)	2% (20 mg ml ⁻¹)	3% (30 mg ml ⁻¹)
Mixtures ^a (w/v%)	1% (10 mg ml ⁻¹)	0.75% (7.5 mg ml ⁻¹)	0.5% (5.0 mg ml ⁻¹)	0.75% (7.5 mg ml ⁻¹)

^aMixtures contained the four test chemicals with the listed concentrations.

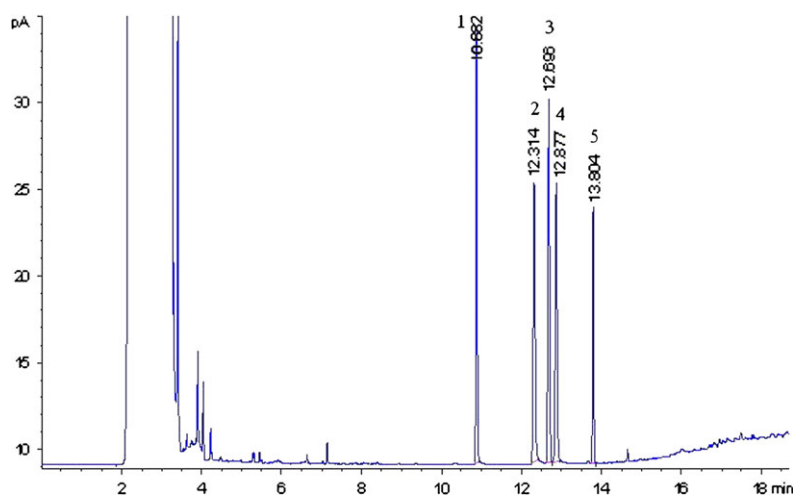


Fig. 1. Chromatogram of four test chemicals and internal standard. Peak 1: OAP (RT = 10.882 min, injected mass = 10 ng), peak 2: PAP (RT = 12.314 min, injected mass = 10 ng), peak 3: PPD (RT = 12.696 min, injected mass = 10 ng), peak 4: MAP (RT = 12.877 min, injected mass = 10 ng), peak 5 (internal standard): biphenyl (RT = 13.804 min, injected mass = 2.5 ng).

plotted versus sampling time. The linear range of the cumulative permeated mass curve was utilized to calculate the SSPR by simple linear regression analysis, i.e. the slope of the linear range of the curve (Fig. 2). The SSPR is typically adjusted by the exposed area and expressed in the unit, $\mu\text{g cm}^{-2} \text{min}^{-1}$ as in equation (1):

$$\text{SSPR} = \frac{\text{Slope of steady stage } (\mu\text{g min}^{-1})}{\text{Exposed area } (\text{cm}^2)} \quad (1)$$

All statistic analyses were performed by the SPSS Version 14.0 (Chicago, IL, USA). To determine the significance of possible factors, the stepwise linear regression analysis was applied. The criterion for adding or deleting an independent variable was based on the F -statistic when the probability of F to enter was ≤ 0.05 or the probability of F to remove was ≥ 0.1 . Statistical significance was set at $P \leq 0.05$.

RESULTS

Glove physical change

The average initial glove thicknesses of NRL and NP did not significantly change for all challenges at $P \leq 0.05$ (non-parametric Kolmogorov–Smirnov Z -test). The PVC shrank significantly and became inflexible after being exposed to the chemical ethanol challenge solutions. The weight changes of the test specimens, NRL and NP were $< 3\%$. For test chemicals in ethanol solution permeation, the weight of PVC decreased 7.16%. The PVC glove thicknesses and weights decreased much while challenged with the chemical ethanol solutions.

BT and SSPR

Table 2 lists the ranges of BTs and SSPRs of single and mixed chemicals through three gloves from the

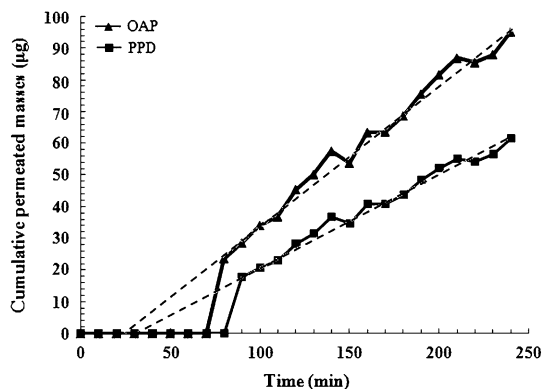


Fig. 2. Cumulative mass permeated versus time curves for OAP and PPD through PVC glove material. The lag time (t_l) was the time-axis intercept from the extrapolation of the steady-state portion of the curve.

triplicate experiments. Among all exposures, the earliest breakthrough was at 40 min for OAP and PPD in the ethanol solutions while challenging the PVC gloves. The BTs of the NRL glove materials were longer than those of PVC gloves for the four chemicals in ethanol solutions. For both NRL and PVC gloves, longer BTs for chemicals in hydrogen peroxide solutions were observed while compared to those in ethanol solutions. In all hydrogen peroxide solutions, only OAP in the cocktail solutions broke through at 140–210 min when challenging the PVC gloves. For the single chemical challenge solutions, PPD had the fastest SSPR for both NRL gloves and PVC gloves. The SSPRs of PVC gloves were higher than those of NRL gloves in all challenge conditions for both single chemicals and mixtures. The PAP did not breakthrough NRL gloves within 4 h. The NP

Table 2. BTs and SSPRs of single and mixed chemicals for three glove types

Gloves	NRL ^a		PVC ^b		NP ^c	
	BT (min)	SSPR ($\mu\text{g cm}^{-2} \text{min}^{-1}$)	BT (min)	SSPR ($\mu\text{g cm}^{-2} \text{min}^{-1}$)	BT (min)	SSPR ($\mu\text{g cm}^{-2} \text{min}^{-1}$)
Ethanol solution						
PAP	>240	NA	110–170	0.05–0.15	>480	NA
MAP	200 to >240	0.14	80–120	0.14–0.22	>480	NA
OAP	60–90	0.14–0.22	40–100	0.28–0.63	>480	NA
PPD	90–120	0.21–0.37	40–60	0.52–0.69	>480	NA
Hydrogen peroxide solution						
PAP	>240	NA	>240	NA	>480	NA
MAP	>240	NA	>240	NA	>480	NA
OAP	>240	NA	>240	NA	>480	NA
PPD	>240	NA	>240	NA	>480	NA
Mixture in ethanol solution						
PAP	>240	NA	140 to >240	0.04–0.06	>480	NA
MAP	>240	NA	>240	NA	>480	NA
OAP	150–200	0.06–0.14	60–90	0.07–0.19	>480	NA
PPD	200–220	0.08–0.1	60–80	0.11–0.18	>480	NA
Mixture in hydrogen peroxide solution						
PAP	>240	NA	>240	NA	>480	NA
MAP	>240	NA	>240	NA	>480	NA
OAP	>240	NA	140 to >240	0.05	>480	NA
PPD	>240	NA	>240	NA	>480	NA

NA, no breakthrough within the 4- or 8-h test periods.

^aAverage measured thickness was 0.1402 ± 0.0065 mm.

^bAverage measured thickness was 0.0897 ± 0.0038 mm.

^cAverage measured thickness was 0.6211 ± 0.0080 mm.

gloves were not permeated by any tested substances during 8-h exposure.

Cumulative permeated mass

Table 3 lists the total cumulative permeated masses for the NRL and PVC gloves. For NRL gloves, the total cumulative permeated masses of the three breakthrough chemicals in ethanol solutions were, in a decreasing order, PPD > OAP > MAP. For PVC gloves, the total cumulative permeated masses of the four breakthrough chemicals in ethanol solutions were, in a decreasing order, PPD > OAP > MAP > PAP. The cumulative permeated masses of PVC gloves were larger than those of NRL gloves. For mixture solutions, the only breakthrough chemical was OAP for PVC gloves, with a total cumulative mass of 31.05 μg .

Predictor analyses of the permeation parameters

Perkins (1990) demonstrated that the chemical concentration (C), molar volume (MV) and octanol–water partition coefficient ($\log K_{ow}$) affect permeation behavior. All these parameters, C , MV and $\log K_{ow}$, were tested as independent variables to explain the results for BTs and SSPRs from different

Table 3. Total permeated masses of breakthrough chemicals for the NRL and PVC gloves

Gloves	NRL Mean \pm SD (μg)	PVC Mean \pm SD (μg)
Ethanol solution		
PPD	154.43 \pm 9.16	507.20 \pm 18.15
OAP	123.93 \pm 9.60	429.51 \pm 162.64
MAP	40.20 ^a	148.54 \pm 58.63
PAP	NA ^b	75.85 \pm 22.53
Mixture		
PPD	41.15 \pm 15.21	130.96 \pm 32.21
OAP	33.42 \pm 7.72	125.56 \pm 56.46
MAP	NA ^b	NA
PAP	NA	39.91 ^a
Hydrogen peroxide solution		
Mixture		
OAP	NA ^b	31.05 ^a

^aThe breakthrough were observed in two of the three experiments.

^bNA, no breakthrough within the 4-h test periods.

challenge conditions. Table 4 shows the statistically significant predictors of permeation parameters with the square of the correlation coefficient (r^2) and

Table 4. Correlation analyses of permeation parameters of the NRL and PVC gloves

Equation	r^2
NRL (BT: $n = 14$ and SSPR: $n = 12$)	
BT = $-3310.538 (C) + 222.246$	0.570 ($P < 0.05$)
BT = $-3578.136 (C) + 3.385 (MV) - 82.698$	0.916 ($P < 0.05$)
$\log(\text{BT}) = -10.598 (C) + 2.372$	0.540 ($P < 0.05$)
$\log(\text{BT}) = -11.452 (C) + 0.011 (MV) - 1.399$	0.865 ($P < 0.05$)
SSPR = $5.216 (C) + 0.041$	0.681 ($P < 0.05$)
$\log(\text{SSPR}) = 14.769 (C) - 1.19$	0.761 ($P < 0.05$)
PVC ($n = 17$)	
BT = $2.613 (MV) - 155.938$	0.427 ($P < 0.05$)
BT = $4.038 (MV) + 52.107 (\log K_{ow}) - 307.61$	0.742 ($P < 0.05$)
$\log(\text{BT}) = 0.011 (MV) + 0.851$	0.368 ($P < 0.05$)
$\log(\text{BT}) = 0.018 (MV) + 0.256 (\log K_{ow}) + 0.108$	0.721 ($P < 0.05$)
SSPR = $15.594 (C) - 0.092$	0.709 ($P < 0.05$)
$\log(\text{SSPR}) = 27.362 (C) - 1.349$	0.651 ($P < 0.05$)
$\log(\text{SSPR}) = 22.187 (C) - 0.014 (MV) + 0.068$	0.784 ($P < 0.05$)
$\log(\text{SSPR}) = 18.51 (C) - 0.022 (MV) - 0.258 (\log K_{ow}) + 1.037$	0.878 ($P < 0.05$)

BT (minutes); C, concentration (w/v%); MV (molecule weight/density, $\text{cm}^3 \text{mole}^{-1}$); n , number of observations.

probability P -values for two tested gloves in ethanol solutions. For NRL gloves, six significant correlations were obtained. The followings were regression results with high r^2 values for BTs and SSPRs (see Table 4 footnote for units):

$$\text{BT} = -3578.136(C) + 3.385(MV) - 82.698$$

$$r^2 = 0.916(n = 14). \quad (2)$$

$$\log(\text{SSPR}) = 14.769(C) - 1.19$$

$$r^2 = 0.716(n = 12). \quad (3)$$

The chemical concentrations in the challenge solutions significantly affected the BT and SSPR in the logarithm transform, $\log(\text{SSPR})$. For a particular tested chemical, the BT shortened and $\log(\text{SSPR})$ accelerated when the concentration of this particular chemical in the challenge solution increased. The effect of MV was only significant for BT, as shown in equation (2). MV and $\log K_{ow}$ were not included as the predictors of SSPR statistically may due to the limited sample size. The significant effects of MV and $\log K_{ow}$ on permeation parameters have been demonstrated in peer studies (Lin and Que Hee, 1998b,c).

Eight statistically significant models were established for PVC gloves. Equations (4) and (5) generated the most significant correlations for BT and $\log(\text{SSPR})$, respectively.

$$\text{BT} = 4.038(MV) + 52.107(\log K_{ow}) - 307.61$$

$$r^2 = 0.742(n = 17). \quad (4)$$

$$\log(\text{SSPR}) = 18.51(C) - 0.022(MV)$$

$$- 0.258(\log K_{ow}) + 1.037$$

$$r^2 = 0.878(n = 17). \quad (5)$$

MV and $\log K_{ow}$ together explained 74% of the variability of BT. Chemical concentration (C), MV, and $\log K_{ow}$ explained 87.8% of the variation of the SSPR in the logarithm transform (i.e. $\log(\text{SSPR})$). The effects of MV and $\log K_{ow}$ were significant in BT and SSPR for PVC gloves, but insignificant for NRL gloves.

DISCUSSION

The ability of three gloves to withstand four ingredients common in hair dyes was tested by exposing the gloves to individual chemicals and mixtures of the chemicals in ethanol and hydrogen peroxide solutions. No breakthrough in an 8-h test indicates potentially complete protection should hairdressers have a continuous 8-h shift. All NP glove withstood exposure for 8 h. All NRL gloves had a BT ≥ 60 min. Thus, the hairdressers must change NRL gloves once they finish the dyeing process, which usually takes 1 h. The PVC gloves had a BT < 60 min. Hairdressers should be informed of this short BT and change gloves frequently. In terms of the BTs and SSPRs, the NRL gloves provide better protection than PVC gloves for four tested chemicals. Lind *et al.* (2007) found that NRL gloves provided better protection than PVC for gloves when challenged with 5% PPD, which is similar to experimental results obtained by this study. However, glove thicknesses varied even when gloves were of the same type.

Two coefficients, diffusion coefficient (D) and permeability coefficient (P), reveal the protecting effect of glove material independent of the thickness. The D ($\text{cm}^2 \text{min}^{-1}$) can be calculated from $D = L^2/6t_l$, where L is the thickness of glove material and t_l is the lag time which is given by the time-axis intercept from the extrapolation of the steady-state portion of the cumulative permeation curve (Fig. 2) (Perkins, 1990). In this study, the D s of PPD were 4.02×10^{-7} for NRL and 4.04×10^{-7} for PVC. The D s of OAP were 5.07×10^{-7} for NRL and 4.14×10^{-7} for PVC. The P ($\mu\text{g cm}^{-1} \text{min}^{-1}$) is the product of SSPR and L (Chao *et al.*, 2007). The P s of PPD were 3.78×10^{-4} for NRL and 5.09×10^{-4} for PVC. The P s of OAP were 2.32×10^{-4} for NRL and 3.58×10^{-4} for PVC. NRL gloves should be more efficient in preventing the skin exposure to the hair dye chemicals while comparing to PVC gloves due to the slightly small values of these two coefficients.

These experimental data are the first published that show the hydrogen peroxide did not accelerate the hair dye permeation through gloves. No data are available in literature for the permeation through gloves of mixtures of four chemicals and chemicals in hydrogen peroxide solutions. Only OAP broke through the PVC glove after 2 h (BT = 140–210 min). Monticello and Gaber (1999) reported that PVC gloves 0.11 mm thick provided ≤ 30 min of protection to 7.5% hydrogen peroxide. The NRL gloves (0.42 mm thick) and NP gloves (0.38 mm thick) provided excellent protection throughout the 8-h tests. The thickness of PVC gloves of this study was same as that in the study by Monticello and Gaber, even though the gloves were obtained from different manufacturers. Hydrogen peroxide may have permeated the PVC gloves during the tests if the permeation behaviors were similar to that of the PVC gloves in the study by Monticello and Gaber. This study did not investigate the permeation of hydrogen peroxide and no measurements were performed. The co-solvent effect of 12% hydrogen peroxide was not identified based on study findings. Lind *et al.* (2004) confirmed the oxidation process for 12% hydrogen peroxide by mixing PPD and MAP, 2.5% of PPD and 17% of MAP remained after 60 min. As the concentrations of the challenge chemicals were identified as a significant predictor of permeation behavior (Table 4), no major breakthrough was observed due to the decrease of the chemical concentrations of the challenge solutions. This explains why no significant permeation was observed when chemicals were dissolved in the hydrogen peroxide solution.

Table 4 shows the statistically significant predictors of permeation parameters for the NRL and PVC gloves. The chemical concentrations in the challenge solutions (C) significantly affected the BT and SSPR for the NRL gloves, but only significantly affected SSPR for PVC gloves. This finding is also based on the BTs (Table 2). The challenge concentrations of PPD were 4% in the single chemical and 1% in cocktail solutions; the range of BTs was 40–60 min for the 4% PPD and 70–80 min for the 1% PPD. A similar phenomenon existed for OAP. An increased challenge concentration of a particular chemical typically yielded an increased cumulative permeated mass (Table 3). For instance, the initial PPD concentration in the single chemical challenge solution was four times that in the mixture challenge solution (4 versus 1%) and the means of the total cumulative permeated masses of these two challenge solutions were proportionally related. The proportional relationships were 154.43 versus 41.15 μg for the NRL glove tests and 507.2 versus 130.96 μg for PVC glove tests. These experimental data demonstrated that the initial mass of a chemical in challenge solution influences permeated mass.

The MV was a significant factor for BTs for the glove materials, NRL and PVC. The small molecules with small MV values move rapidly and tend to breakthrough the glove quickly according to the chromatographic model (Que Hee, 1996). This rapid breakthrough resulted in MV being a positive factor in predicting BT. Along a similar line, MV affected the SSPR negatively, implying that large molecules move slowly within glove material, resulting in a low SSPR.

The $\log K_{ow}$, a surrogate of the chemical polarity, was also a significant factor affecting BT and SSPR. According to the liquid–liquid partition model, a chemical permeates a glove material rapidly when the polarities of the challenge chemical and the polymer (glove material) are similar (Que Hee, 1996). The $\log K_{ow}$ was positively correlated with BT and negatively correlated with SSPR in the PVC glove tests. Notably, PPD, a hydrophile chemical with a negative $\log K_{ow}$ value, broke through fast at a high permeation rate when the PVC acted as a relative polar solvent. The significance of polarity was not observed for the NRL glove implying that the glove material itself has a significant role in permeation behavior. When all possible factors were involved, the significance of certain factors was decreased by other factors. To extrapolate these results to different challenge combinations should be conservative due to the limited sample size.

Evans *et al.* indicated that the temperature differential between the inside and outside of gloves adversely affected chemical BT and the permeation rate of a solvent passing through the glove material (Evans *et al.*, 2001). Thus, when dyeing hair, the hair dye permeation process occurred at the temperature higher than this test temperature as hairdressers wear gloves. The temperature of the glove inside surface should rise rapidly when contacting the hairdresser's skin. The BTs and permeation rates in practice shall be underestimated by the current experimental settings.

Commercial hair dyes are formulated using dozens of ingredients and varied for different colors and manufacturers. Commercial hair dyes are typically creams; however, challenge solutions of this study were liquid. Ethanol was able to shorten the BT of 2-hydroxyethyl methacrylate for PVC gloves (Andreasson *et al.*, 2003). Ethanol therefore interferes with the permeation behavior of PVC. The essential permeation parameters of different glove materials reported comprise a reliable reference for glove selection.

In conclusion, disposable NRL gloves and disposable PVC gloves cannot be used repeatedly when in contact with hair dyes. NP gloves are safe for at least 8 h. Low concentrations of chemical in challenge solution delayed BT and decreased the SSPR. The compositions of challenge solutions and physical and

chemical properties (MV and $\log K_{ow}$) affected the ability of different gloves to withstand permeation. Hydrogen peroxide did not accelerate the chemical BT.

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