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Enhanced migration of plasticizers from polyvinyl chloride consumer products through artificial sebum

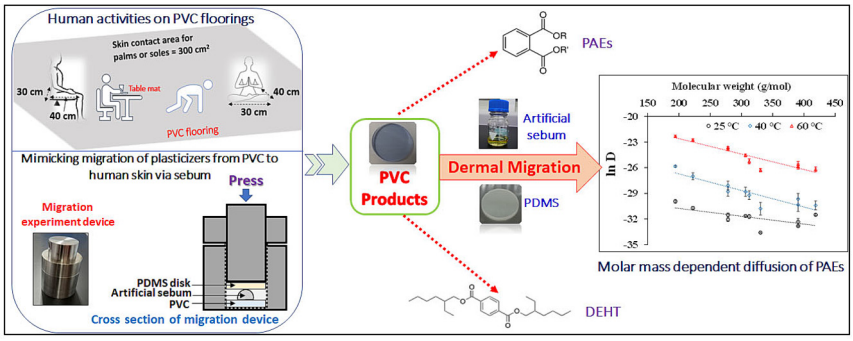
Rishikesh Bajagain [a], Gayatri Panthi [a], Joung-Ho Park [a], Jae-Kyoung Moon [a], Jihye Kwon [b], Du Yung Kim [c], Jung-Hwan Kwon [c], Yongseok Hong [a,*]

[a] Department of Environmental Engineering, Korea University Sejong Campus, 2511 Sejong-ro, Sejong City 30019, Republic of Korea
[b] Department of Environmental Engineering, Daegu University, Gyeongsan 38453, Republic of Korea
[c] Division of Environmental Science and Ecological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

HIGHLIGHTS

- Dermal migration of PAEs from PVC plastics via artificial sebum is assessed.
- Diffusion and migration are increased with sebum mass and temperature, while decreased with pressure and molar mass of PAE.
- Diffusion of DINP in soft PVC (cPVC) is higher than hard PVC (mPVC) sample tested.
- There is a potential risk of exposure to PAEs from household PVC articles via skin.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, the migration of plasticizers from modeled and commercial polyvinyl chloride (mPVC and cPVC, respectively) to poly(dimethylsiloxane) via artificial sebum was assessed to mimic the dermal migration of plasticizers. In addition, the various factors affecting migration of phthalic acid esters (PAEs) from diverse PVC products were investigated. The migrated mass and migration ratio of PAEs increased but the migration rate decreased over time. The migration rate increased with sebum mass, contact time, and temperature but decreased under higher pressure. Low-molecular-weight PAEs (dimethyl phthalate and diethyl phthalate) migrated in higher amounts than high-molecular-weight PAEs (dicyclohexyl phthalate [DCHP] and diisononyl phthalate [DINP]). Diffusion of all PAEs in mPVC increased with temperature, with diffusion coefficients ranging from 10^{-13} to 10^{-15}, 10^{-12} to 10^{-14}, and 10^{-10} to 10^{-12} $cm^2 \cdot s^{-1}$ at 25 °C, 40 °C, and 60 °C, respectively; the enthalpy of activation ranged between 127 and 194 $kJ \cdot mol^{-1}$. Moreover, migration depended on total PAE content of the product, as the diffusion coefficient for DINP in cPVC (softer PVC) was approximately three orders of magnitude higher than that for DINP in mPVC (harder PVC); this may be due to the increase in free volume with increasing plasticizer content. Finally, the daily exposure doses of the plasticizers were estimated. These findings will be helpful for estimating dermal exposure risk.

1. Introduction

Plasticizers are additives that have been extensively used for the softening of plastic products, which may comprise 15–50 % mass of the product (Chaudhary et al., 2016; Olkowska and Gržinić, 2022) and 10–70 % by mass of additive, of which about 80 % of plasticizers are used in polyvinyl

* Corresponding author.
E-mail address: yongseokhong@korea.ac.kr (Y. Hong).

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chloride (PVC) and remaining 20 % in cellulose plastics (Hahladakis et al., 2018; Hansen et al., 2013; Yan et al., 2021). Besides, phthalic acid esters (PAEs) or phthalates are the most widely consumed plasticizers, which accounted about 80 % volume of the global plasticizer consumption (Al-Natsheh et al., 2015). Interestingly, the global demand for PVC is approximately 17 % (ranked 3) of all plastic products (Hahladakis et al., 2018), and PAEs are widely reported in PVC products, including children's articles (Al-Natsheh et al., 2015; Babich et al., 2020; Bouma and Schakel, 2002; Gill et al., 2010; Gimeno et al., 2014; Kim et al., 2020; Xie et al., 2015). Some PAEs are recognized as endocrine disruptors, showing various toxic effects and associated with decreased fecundity, pregnancy loss, and adverse obstetric outcomes (Fabjan et al., 2006; Grindler et al., 2018; Net et al., 2015).

The probability of PAEs being released from products into the environment and entering the food chain is very high because they are not chemically bound to the polymer structure (Bajagain et al., 2023; Hou et al., 2021; Net et al., 2015; Sajiki and Yonekubo, 2003; Yan et al., 2021). Therefore, the potential consequences and risks associated with human exposure to PAEs may be challenging, because of the abundance of PVC-based consumer products, which increases environmental concerns regarding PAEs as possible health hazards (Al-Natsheh et al., 2015; Hou et al., 2021; Howdeshell et al., 2008; Wong et al., 2010). Though food is a major contributor for exposure to PAEs by oral, contributing >67 % of human exposure (Das et al., 2014); PAEs can migrate into the human body via inhalation, or dermal pathways (Clark et al., 2011; Coltro et al., 2014; de Anda-Flores et al., 2021; Kang et al., 2021; Lyche, 2011; Ouchi et al., 2019; Sugeng et al., 2020; Takehisa et al., 2005). PAEs have been detected in urine samples collected from pregnant women, which possibly migrated from ingestion, inhalation, and dermal absorption (Sugeng et al., 2020). When in contact with the human skin, PAEs can migrate from consumer products through the epidermis; thus, dermal migration is an important exposure route. A recent dermal exposure study suggested that the highly lipophilic phthalates may transport easily across the stratum corneum lipids (Sugino et al., 2017). Increased use of PVC products for various purposes, such as PVC flooring, table covers, toys, packaging or greenhouse films, medical articles, wires or cables, fluid bags, and cosmetic products (Earls et al., 2003; Gimeno et al., 2014; Lyche, 2011; Sugeng et al., 2020; Yan et al., 2021), has rendered PVC a good candidate for application in experimental migration tests.

Most migration studies have been conducted using organic solvents or aqueous media as food simulants (Clausen et al., 2015; Coltro et al., 2014; de Anda-Flores et al., 2021; Ge et al., 2021; Kim et al., 2003; Takehisa et al., 2005; Yuan et al., 2020), which may lead to the overestimation of results because a higher amount of target chemicals may be leached out into those solvent media than the actual expected migration in real condition. For instance Ge et al. (Ge et al., 2021) studied the dermal sorption of chemicals, including PAEs, from pad products using artificial sweat as a simulant. Additionally, majority of the previous studies on the migration of contaminants from consumer products were conducted under harsh conditions, that is, by placing the products into solvents and then extracting the contaminants (Coltro et al., 2014; de Anda-Flores et al., 2021). Meanwhile, Ouchi et al. (2019) conducted a dermal migration experiment by directly contacting a PVC sheet with a sampler (polyethylene, PE) without using any medium. However, PVC was pressed with two PE sheets (top and bottom), which is less likely to be relevant under environmental conditions. Furthermore, most studies only analyzed the migrated concentration for contaminants of concern, and the risk assessment for these compounds remains unexplored (Bernard et al., 2015; Coltro et al., 2014; de Anda-Flores et al., 2021; Frederiksen et al., 2016; Xie et al., 2015). In addition, several parameters can affect the migration rate of compounds, such as contact time, temperature, concentration of chemicals in products, migration medium, molar mass, branching, polarity, and surrounding matrix; thus, experimentally measured migration rates under certain conditions cannot be applied to other conditions (García Ibarra et al., 2019; Gong et al., 2014; Marcilla et al., 2008; Zeng et al., 2019). Therefore, typical dermal migration tests do not mimic realistic conditions.

Sebum present in the human skin acts as a carrier for these compounds to migrate from products and can therefore affect migration rates (Frederiksen et al., 2016; Kim et al., 2022). In contrast, Schneider et al. (2016) showed that sebum did not enhance the dermal penetration and intradermal reservoir of epidermally applied chemicals (ethanol and toluene). Moreover, studies on the sebum-mediated migration of phthalate/non-phthalate additives from PVC products are scarce. Recently, sebum was shown to mediate the migration of plasticizers from PVC products (Kim et al., 2022) which is more relevant to the real conditions; however, the effects of sebum mass, applied pressure, and molar mass of phthalates on migration remain unexplored. Therefore, the present study investigated the migration of different plasticizers from laboratory prepared or modeled PVC (mPVC) and commercial PVC (cPVC) products via artificial sebum under various conditions (i.e., sebum mass, contact time, temperature, pressure, and PVC product type), which is expected to be more closely mimic the real environment. We used poly(dimethylsiloxane) (PDMS) to quantify the migrated amount of phthalates from PVC products, as PDMS has been widely used as a passive sampler for hydrophobic organic pollutants (Angel et al., 2022; Kwon et al., 2007; Posada-Ureta et al., 2017; Vrana et al., 2005).

The major objective of the present study was to investigate the migration of PAEs from various PVCs to PDMS via an artificial sebum to mimic the possible dermal transfer of PAEs into the human body. Specifically, we evaluated the effect of artificial sebum mass, contact time, temperature, and pressure on the migration of phthalates from mPVC. Diffusion coefficient and activation enthalpy of different phthalates in mPVC were determined using Fick's law of diffusion and van't Hoff's equations, respectively. The diffusivity of mPVC and cPVC was compared. Furthermore, the daily exposed dose for different plasticizers from all PVCs was evaluated. Our results can be used to predict the potential health risks of dermal migration of various plasticizers from plastic products into the human body via sebum.

2. Materials and methods

2.1. Reagents

Phthalates purchased from Alfa Aesar included dimethyl phthalate (DMP, Germany), diethyl phthalate (DEP, India), dibutyl phthalate (DBP, USA), diisobutyl phthalate (DIBP, Japan), di–n–pentyl phthalate (DNPP, Great Britain), benzyl butyl phthalate (BBP, Great Britain), di(2–ethylhexyl) phthalate (DEHP, Colombia), dicyclohexyl phthalate (DCHP, Japan), di-n-octyl phthalate (DNOP, Japan). Benzyl benzoate (BB, India), and tetrahydrofuran (THF, USA) were also purchased from Alfa Aesar. Diisononyl phthalate (DINP) was purchased from Sigma-Aldrich (Netherlands) and di(2-ethylhexyl) terephthalate (DEHT) from Acros Organics (USA). Certified reference material (CRM 113–03–006) for different phthalates was purchased from the Korea Research Institute of Standards and Science (KRISS). DCM and n-hexane were obtained from Daejung (Siheung, Republic of Korea) and methanol from Sigma-Aldrich (St. Louis, MO, USA). The physicochemical properties of plasticizers used in the present study are listed in Table S1.

2.2. Preparation of PVC and PDMS disks

The present study used two types of PVCs for migration experiments: mPVC prepared in the laboratory and cPVC obtained from the market. mPVC films (0.2–mm thick, see Fig. S1A) were prepared in the laboratory using the tetrahydrofuran (THF) dissolution method, as described in the literature (Takehisa et al., 2005; Yan et al., 2021). Briefly, pure PVC powder (Sigma Aldrich, China) was dissolved in THF using magnetic stirrer until a clean PVC solution was formed, then 10 PAEs mixture was added and stirred for 3 h at 500 rpm. The PVC solution was then transferred into clean glass petri dish and allowed to evaporate the THF solvent (see the details of mPVC film preparation in Text S1). In addition, three commercial PVC products of different thicknesses (cPVC–1 = 0.2 mm thick; cPVC–

2 = 0.3 mm thick, and cPVC–3 = 4.25 mm) were purchased from an online store (FilmBank, Korea).

The initial concentrations of various plasticizers in both PVCs were analyzed using gas chromatograph-mass spectrometer (GC–MS); the results are summarized in Table S2. The initial concentration of nine different phthalates were ranged from 11,486 (lowest for DMP) to 15,216 μg/g (highest for BBP) and 130,812 μg/g for DINP (since DINP was spiked at the concentration of 10 times higher than other nine PAEs). The % recovery of different phthalates are ranged from 95.7 % (for DMP) to 126.8 % (for BBP) with overall recovery of 109.6 %. A relatively higher concentration for higher molecular PAEs was found in mPVC which is may be due to their longer carbon chains in phthalate rings, low vapor pressure and solubility and higher boiling points compared to lower molecular PAEs, resulting no mass loss during spiking and recovery procedures. In addition, the different plasticizers (DEHT and DINP) were quantified in cPVC samples (see Table S2). The peaks appeared when injecting cPVC extract in GC–MS for other plasticizers were not quantified due to unavailability of the chemicals for calibration.

Furthermore, PDMS sheet with thickness of 1–mm (HSW Co., Ltd., Korea) was cut into 40 mm-diameter disks (Fig. S1B) by using 40–mm hollow punch. The custom–cut PDMS disks were cleaned by using soap water, deionized water and organic solvents viz. methanol, hexane and dichloromethane (DCM) sequentially in glass bottles with aluminum foil-lined caps. During each solvent cleaning, the glass bottles containing PDMS disks were cleaned with ultra-sonication for 30 min and transferred in horizontal shaker at 250 rpm for 24 h. The cleaned PDMS disks were stored in methanol which were then dried in fume hood and oven prior to use.

2.3. Plasticizer migration experiment

In the present study, artificial sebum was used to mimic the migration of phthalates from PVC upon coming in contact with the human skin via sebum produced in the epidermis. Table 1 shows the constituents used for preparation of artificial sebum in the laboratory along with vitamin E for longer stability, as suggested in the literature (Kim et al., 2022; Stefaniak et al., 2010; Wertz, 2009). A migration device was used to conduct the migration experiment, as described in Text S2. Briefly, artificial sebum was dropped at the center of a clean PDMS disk and sandwiched between the PDMS disk and a PVC film. Then, a set of disks was placed inside the well of the migration device such that the PVC film was set at the bottom of the well and PDMS at the top (Fig. S2). Then, a mass load (~700 g weight) was introduced inside the well to press PDMS/PVC (diameter = 40 mm), which exert a pressure of 5.5 kPa and the device was incubated. In this way, we simulated the actual pressing of PVC by human body when PVC get contacted with the skin. At different time intervals, both the PDMS disk and PVC film were carefully removed using clean metal forceps, rinsed with deionized water, wiped with a tissue, and analyzed for PAEs. Moreover, different factors affecting the dermal migration of plasticizers (sebum mass, temperature, pressure, and PVC product type) from PVC (see Text S3) were evaluated. All experiments were performed with three to five replicates.

PAEs and other plasticizers in PVC and PDMS were extracted with DCM using the ultrasonication method and analyzed using gas chromatography (Agilent 6890 N GC) coupled with a mass spectrometer (Agilent 5973 MSD) (GC–MS) with a DB–5 capillary column (Agilent, 30 m × 250 μm × 0.25 μm) and an autosampler (Agilent 7683). Table S3 presents the retention times and the characterization and quantification results of ions in various plasticizers. PVC extract was filtered via a Florisil column (glass Pasteur pipet packed with glass wool (8–15 μm, Chemglass Life Sciences, Germany) and Florisil® (<200 mesh, Supelco, USA)) and injected into GC–MS. Recovery data was determined using 7–point calibration curves (with R^2 >0.99) for all PAEs. A good extraction recovery (84.2–100.8 %) was achieved for various phthalates in PVC certified reference material (CRM) using this method, as shown in Table S4. In addition, chromatograms for 10 phthalates used for preparing mPVC and the internal standard (benzyl benzoate) are shown in Fig. S3. Furthermore, different types of PVCs were analyzed for total phthalate or plasticizer content using evolved gas analysis coupled to mass spectrometry (EGA–MS) and thermal desorption-gas chromatography coupled to mass spectrometry (TD–GC/MS). The Cl content of PVC samples was analyzed using combustion ion chromatography (CIC). Text S4 and S5 describe the details of the analysis of plasticizer (phthalates/non-phthalates) concentration in PDMS and PVC samples, total plasticizer concentration, and Cl content of all PVC samples.

Table 1
Constituents of artificial sebum prepared in the laboratory and mass of each components to prepare 1 g of artificial sebum.

Constituent	Chemical	Mass (mg)	Weight %	Manufacturer
Squalene	Squalene	124	12.4	Acros Organics, France
Wax monoester	Jojoba oil	250	25.0	Sigma Aldrich, Israel
Triglyceride	Triolein	446	44.6	Alfa Aesar, China
Fatty acid	Oleic acid	170	17.0	Alfa Aesar, USA
Vitamin E	±α-tocopherol	10	1.00	Sigma Aldrich, Germany

2.4. Theory and models

The mass of plasticizers (microgram of target compounds) migrating from PVCs to the PDMS was quantified using GC–MS. The mass of each PAE migrating from mPVC was plotted as a function of time at different temperatures. In addition, Ge et al. (Ge et al., 2021) calculated the dermal migration ratio for each PAEs. The migration ratio (r, %) of phthalates from PVC products to PDMS was calculated as follows:

$$r = \frac{m_{PDMS}}{m_{PVC0}} \times 100\% \quad (1)$$

where m_{PDMS} is the mass of compound migrating into the PDMS disk (μg) and m_{PVC0} is the initial mass of the compound in the PVC film (μg).

The migration ratio of each compound is plotted as a function of time at different temperatures. Furthermore, the dermal migration rate (μg cm^{-2} h^{-1}) was calculated using the migrated mass of phthalate (μg), as follows:

$$\text{Migration rate} = \frac{\text{Migrated mass } (\mu g)}{\text{Migrated area } (cm^2) \times \text{time } (h)} \quad (2)$$

Moreover, the plasticizer concentration in PVC surface after migration can be considered as constant since the plasticized PVC products contain a very high plasticizer content (Kim et al., 2022). Thus, the mass of plasticizer compound migrating through the contact area at time t can be simplified based on Fick's second law of diffusion as follows (Clausen et al., 2015; Crank, 1975; Kim et al., 2022):

$$M_t = 2C_0\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \quad (3)$$

where M_t is mass migrating through the contact area at time t (μg cm^{-2}), C_0 is the initial concentration of plasticizer in the PVC product (μg cm^{-3}), D is the diffusion coefficient (cm^2/ s), and t is the experimental time (s).

The diffusion coefficient of plasticizers in PVC products depends on temperature; therefore, the activation enthalpy of diffusion can be calculated by plotting the natural logarithm of D (lnD) versus the inverse of temperature (1/T) using the van't Hoff equation, as follows:

$$\ln D = -\frac{H^*}{R} \times \frac{1}{T} + C \quad (4)$$

where T is the absolute temperature (K), H is the activation enthalpy of diffusion (kJ mol^{-1}), R is the gas constant (8.3145 J mol^{-1} K^{-1}), and C is a constant.

In the case of dermal exposure, one can touch the products directly and plasticizers can migrate out of the products and be absorbed through the epidermis. Thus, the dermal migration rate is an important parameter for

assessing exposure to plasticizers. Considering the daily exposure dose (DED) as the maximum potential dermal intake (or absorption) rate by assuming 100 % absorption of migrated PAEs, the DED can be calculated as follows (Ge et al., 2021; Pakalin et al., 2008):

$$\mathrm{DED}\ \left(\mu g\ kg^{-1}d^{-1}\right) = \frac{\overline{MR} \times CA \times t_{exp}}{BW} \quad (5)$$

where $\overline{MR}$ is the time-weighted average migration rate (μg cm^{-2} min^{-1}), CA is the skin contact area (cm^2), t_{exp} is the exposure time in a day (min d^{-1}), and BW is body weight (kg).

The body weight was estimated to be 60 kg for adults (Ge et al., 2021; Pakalin et al., 2008), whereas the skin contact area for palms or soles and exposure time were set to 300 cm^2 and 60 min d^{-1}, respectively (Kim et al., 2022).

2.5. Statistical analysis

The data were entered into an Excel file (Microsoft Office Excel, 2019) to calculate descriptive statistics (mean; and standard deviation, SD). These data were used in one-way ANOVA analysis, and the significant differences of the mean values at $p < 0.05$ were determined through the Tukey (honestly significant difference) test using OriginPro 8.5 software.

3. Results and discussion

3.1. Dermal migration of PAEs from mPVC

3.1.1. Effect of sebum mass on the migration of PAEs from mPVC

The effect of artificial sebum mass on the migration of PAEs from mPVC was evaluated at different sebum masses (0, 1, 2, 4, and 6 mg·cm^{-2}) at 25 °C for 48 h. A constant contact area between PVC and PDMS (12.56 cm^2) was ensured throughout the experiment. The masses of artificial sebum used in the present study were in the range of mass of naturally secreted sebum in the human skin, i.e. (Downing et al., 1981; Mukherjee et al., 2016; Stewart et al., 1984). As shown in Fig. 1, the mass of each PAE migrating to the PDMS increased with increasing mass of the artificial sebum. The sebum may facilitate the physical preconditioning for the migration of PAEs from PVC surface. This is because artificial sebum contains constituents composed of organic compounds that act as the carrier medium for PAE migration. Interestingly, it is argued that the artificial sebum gets absorbed by PVC, further plasticizing PVC (Kim et al., 2022). Overall, PAE migration was minimal at 0 mg·cm^{-2} sebum (i.e., PVC in contact with PDMS without artificial sebum); however, it gradually increased up to 4 mg·cm^{-2} sebum and then remained nearly constant. When sebum comes in contact with PVC surface, the lipophilic PAEs tend to dissolve rapidly in sebum and migrate into the PDMS sampler faster than the PVC when contacted without sebum (Kim et al., 2022). Thus, sebum present in the human skin can act as a good medium for physical preconditioning and thereby accelerate the migration of phthalates from PVC.

The migration ratio, that is, the fraction of compounds that migrated from PVC to PDMS (Eq. (1)), for different phthalates ranged from 0.17 % to 1.0 % (Fig. S4A) at ambient room temperature (25 °C). Furthermore, the migration rate increased with increase in sebum mass from 0 to 4 mg·cm^{-2} and was approximately 3 to 38–fold of that in the absence of sebum; subsequently, at 6 mg·cm^{-2}, the migration rate remained near constant (Fig. S4B). The migration rate for DEHP, a widely used phthalate in PVC, was 0.0023, 0.0064, 0.0087, and 0.0134 μg/cm^2/h at 0, 1, 2, 4 mg/cm^2 sebum mass. Therefore, higher sebum mass results in greater phthalate migration; however, at a very high sebum mass, under certain conditions, the migration rate does not increase. Accordingly, further experiments were conducted at a sebum mass of 4 mg·cm^{-2}. In addition, the migration of DMP was the highest (27 μg) and that of DCHP was the lowest (5 μg). From these results, the migration of low-molecular-weight PAEs (DMP and DEP) was significantly higher than that of high–molecular weight PAEs. At the sebum mass of 0 mg·cm^{-2}, the migration of DMP, BBP, DEHP, and DINP was higher than that of the other PAEs.

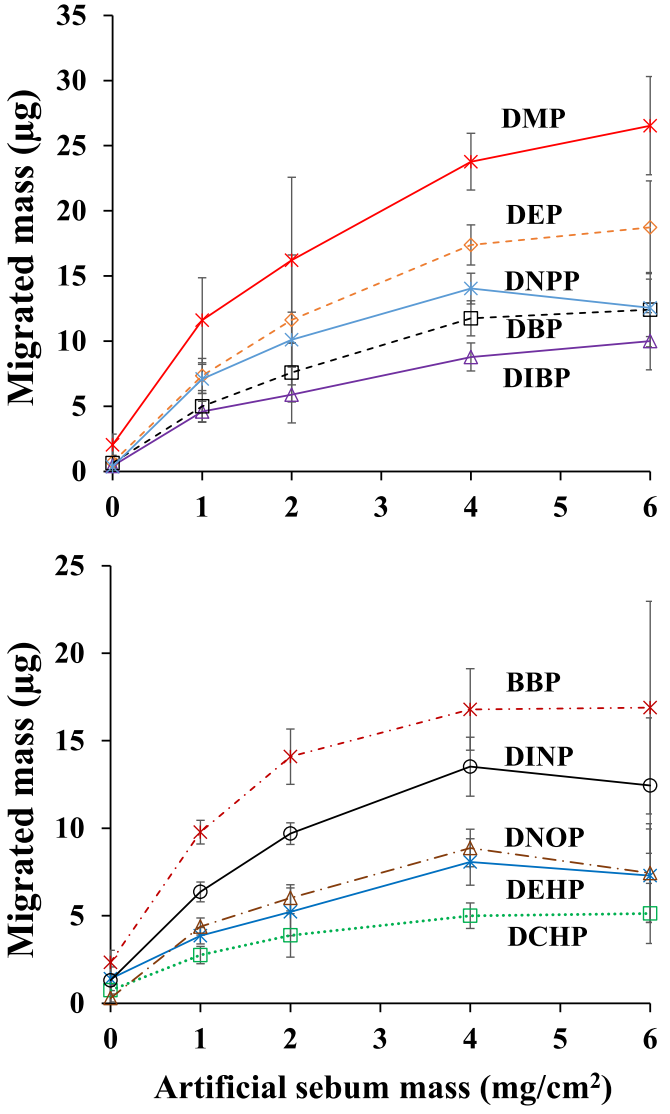


Fig. 1. Effect of sebum mass on the dermal migration of various phthalates (at 25 °C) from modeled polyvinyl chloride (mPVC). Normalized mass is plotted for diisononyl phthalate (DINP).

3.1.2. Effect of contact time and temperature on the migration of PAEs from mPVC

The migration of all PAEs from mPVC gradually increased with contact time at all temperatures (Fig. S5). When the contact time increased from 1.5 to 72 h, the migration of PAEs increased by 3.4–13.4 fold, 2.2–9.1 fold, and 14.4–45.3 fold at 25 °C, 40 °C, and 60 °C, respectively. In addition, temperature significantly affected the migration of PAEs from mPVC. When temperature increased from 25 °C to 40 °C, the mass of migrated PAEs increased from 1.9–fold (the lowest increment for DINP) to 7.6–fold (the highest increment for DMP). Similar results were obtained when temperature increased from 40 °C to 60 °C. The free volume (or space) within the polymer increases with increasing temperature (thermal expansion), which increases the migration of molecules (Comyn, 2021). The overall migrated PAE mass (μg) via artificial sebum was in the following order: DMP > DEP > DBP ≥ DIBP > DNPP > BBP > DNOP ≥ DEHP > DINP ≥ DCHP.

Similar to the migrated mass, the dermal migration ratio (%) increased with time for all PAEs tested. The dermal migration ratio is the ratio

describing the mass fraction of migrated compounds into the receiving medium to the initial mass in consumer products; thus, it is normalized to the initial concentration of the product and better represents the migration tendency of each compound. If migration ratios are not considered, the exposure risk of phthalates via dermal migration is overestimated (Ge et al., 2021), since the mass PAEs migrated from PVC also depends upon initial plasticizer content in PVC. As shown in Fig. S6, the top four phthalates (DMP, DEP, DBP, and DIBP) presented migration ratios in the range of 24–52 %, whereas that for the bottom six phthalates presented 7–16 % in the worst-case scenario (60 °C). Similarly, the migration rate (μg cm^{-2} h^{-1}, using Eq. 2) increased with increasing temperature and decreased with contact time (Fig. S7). The decrease in the migration rate with time is contrary to the trends of migrated mass and migration ratio, which suggest that the diffusion and migration process tend to stall at some time duration. Kim et al. also found a similar trends for migration of plasticizer from PVC articles (Kim et al., 2022).

Furthermore, the migration of low-molecular-weight PAEs (including DMP, DEP, DBP, and DIBP, with up to four carbon atoms in the chain) was significantly higher than that of high-molecular-weight PAEs (those with more than four carbon atoms). The migration of plasticizers is inversely proportional to their molecular weight (Marcilla et al., 2008; Marcilla et al., 2004). The present study also found negative correlations between the migration and molar mass of PAEs (see Fig. S8). In addition, the structure of the carbon chain in phthalates may be responsible for the migration, as DCHP showed the lowest migration results, with two cyclohexane groups in the carbon chain. In addition, DIBP showed a relatively lower migration rate than DBP although the molecular weight for both compounds is same (i.e. 278.34 g·$mole^{-1}$), because of its isomeric carbon chain in DIBP molecule. Similar results were observed for the two isomeric compounds DEHP and DNOP, with DNOP showing a higher migration rate at all tested temperatures. Thus, the physicochemical properties of compounds can affect their migration from the consumer products.

3.1.3. Effect of pressure on the migration of PAEs

The present study demonstrated the effect of pressure applied to PVC on the dermal migration of PAEs from mPVC at three different pressures (5.5, 10.4, and 18.5 kPa). This study intended to evaluate the effect of pressure; i.e. force exerted by human body per unit area of human skin (such as hamstrings and buttock or soles or palms) exposed to PVC; on dermal migration of PAEs. The different pressures were obtained to the mPVC sheets by changing the mass of stainless-steel load keeping a constant contact area of PVC/PDMS at constant atmospheric pressure of ~1 atm and this effect was performed at two different temperatures (25 and 40 °C). The dermal migration of all PAEs unexpectedly decreased when the pressure increased from 5.5 to 10.4 kPa at 25 °C, while it remained constant when pressure was further increased to 18.5 kPa (Fig. 2A). A similar trend was observed for the dermal migration ratio of different phthalates (Fig. S9). A possible reason for the decrease in the migration of PAEs with increase in pressure may be the lower sebum intrusion in PDMS at higher pressures. Furthermore, sebum components (e.g., oleic acid and squalene) that intrude PDMS at different pressures were analyzed, and their concentration was found to decrease remarkably at higher pressure, following the trend of PAE migration (Fig. 3). Pores present in the PDMS sheet, which absorb PAEs

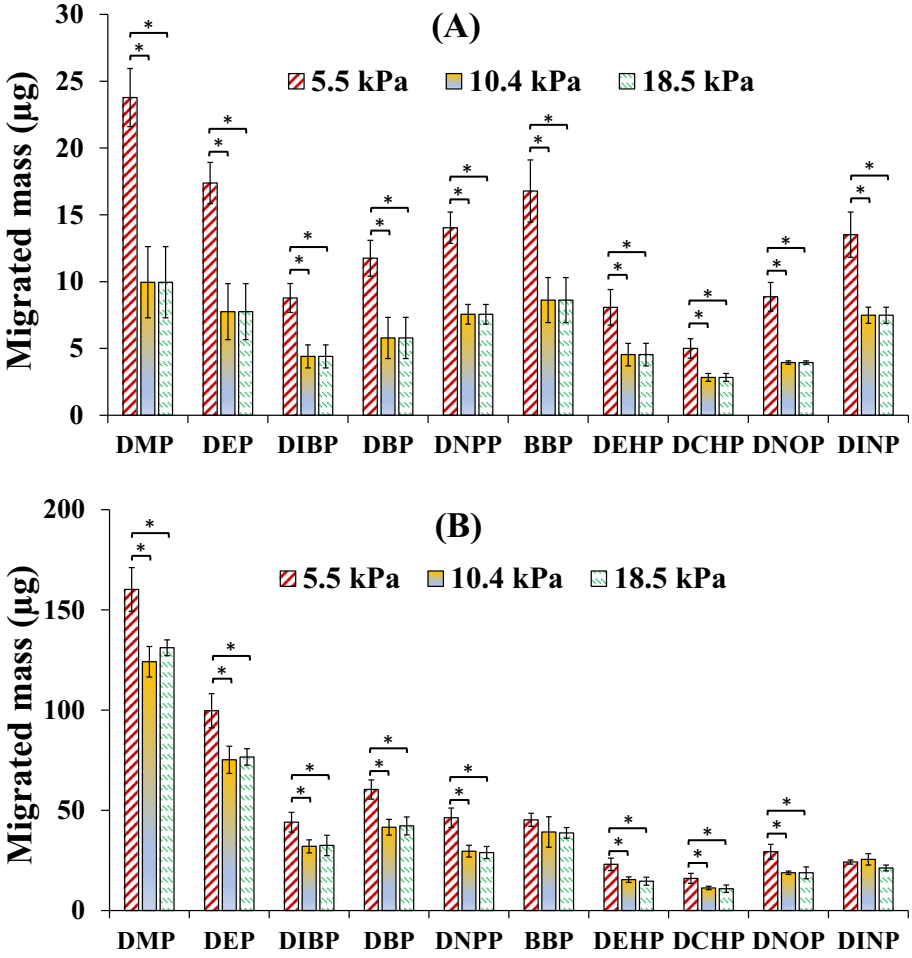


Fig. 2. Dermal migration of phthalates under three different pressures (5.5, 10.4, and 18.5 kPa) at incubation temperatures of (A) 25 °C and (B) 40 °C. The significant differences ($p < 0.05$, Tukey's test) within each PAE at different pressure are marked by an asterisk.

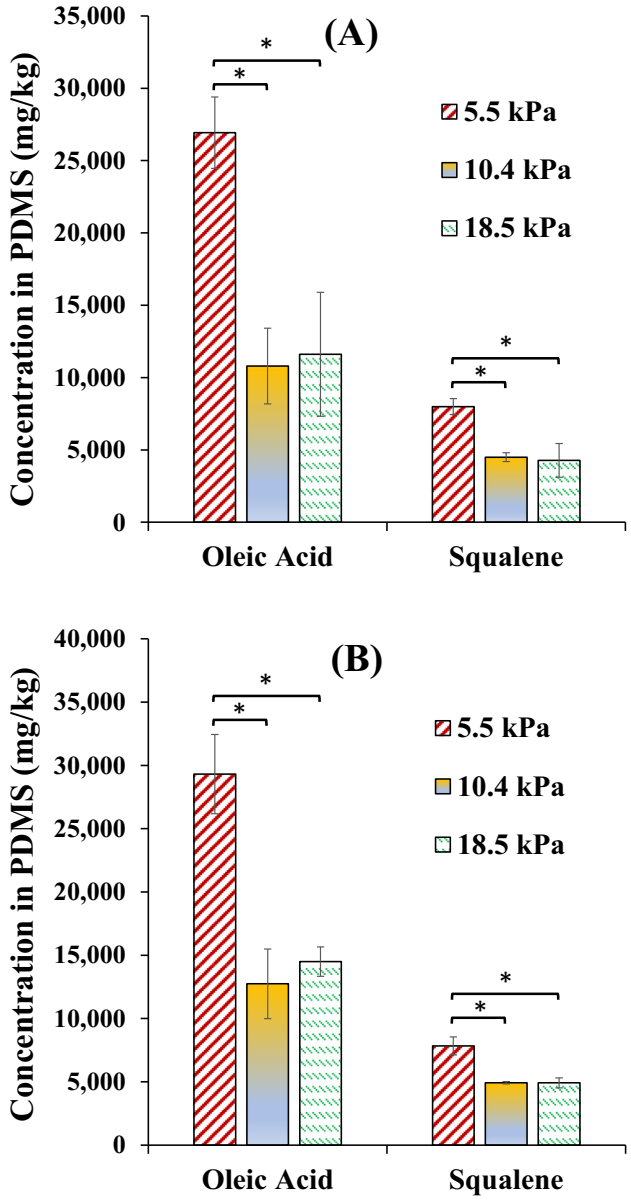


Fig. 3. Concentration of oleic acid and squalene in poly(dimethylsiloxane) (PDMS) under three different pressures (5.5, 10.4, and 18.5 kPa) after incubating the dermal migration devices at (A) 25 °C and (B) 40 °C. The significant differences ($p < 0.05$, Tukey's test) within each PAE at different pressure are marked by an asterisk.

released from PVC, may contract with increasing pressure on the system, lowering the intrusion of chemicals. In addition, pressure affects free volume, as it decreases with increasing pressure, thereby reducing the migration ability (Comyn, 2021). Thus, pores in human skin may shrink at excessive mass under higher pressure, resulting in lower migration rates of phthalates via sebum.

A similar trend was observed at 40 °C for the migration of eight PAEs (i.e. DMP, DEP, DIBP, DBP, DNPP, DEHP, DCHP, and DNOP); however, there were no significant differences in the migrated masses of the BBP and DINP at applied pressures of 5.5, 10.4 and 18.5 kPa (Fig. 2B). Therefore, the migration kinetics of BBP and DINP may be independent of pressure at higher temperature (40 °C), however migrated masses are significantly increased for DCHP (3.2–4.0 times) and DINP (1.8–3.4 times) when the temperature increased from 25 °C to 40 °C at constant pressure. In overall, when temperature increased from 25 °C to 40 °C, the migrated mass of all PAEs increased by 1.8–6.7, 3.4–12.5, and 2.8–13.2 times at 5.5, 10.4 and 18.5 kPa, respectively.

3.2. Diffusion of plasticizers in mPVC and cPVC

The diffusion coefficient and activation enthalpy values of various phthalates in mPVC and cPVC are presented in Table 2. The diffusion coefficients (as determined using Eq. 3) for mPVC were evaluated at 25 °C, 40 °C, and 60 °C, whereas cPVC products were tested at 40 °C alone, which may represent the real environmental scenario. The diffusivity of all PAEs in the artificial sebum increased by 1–3 orders of magnitude with increase in temperature. Increases in diffusivity of similar orders of magnitude have been reported in the literature (Kim et al., 2003; Li et al., 2016; Tüzüm Demir and Ulutan, 2013; Yuan et al., 2020). The low-molecular-weight phthalates showed a higher diffusivity (e.g., the highest for DMP at 25 °C, $D = 1.01 \times 10^{-13}$ $cm^2 \cdot s^{-1}$) than mid-chain PAEs (D in the order 10^{-14} $cm^2 \cdot s^{-1}$) and high-molecular-weight phthalates (the lowest for DINP, followed by DCHP, DEHP, and DNOP, D in the order 10^{-15} $cm^2 \cdot s^{-1}$) (Table 2 and Fig. S10). When temperature increased from 25 °C to 40 °C, the diffusion coefficient increased by 3–60 times, and at 60 °C, the increment was 210–3660 times that at 25 °C. The diffusion coefficients of different PAEs ranged from to 10^{-13} to 10^{-15}, 10^{-12} to 10^{-14}, and 10^{-10}–10^{-12} $cm^2 \cdot s^{-1}$ at 25 °C, 40 °C, and 60 °C, respectively.

In addition, a linear relationship ($R^2 = 0.9254$–0.9998) between ln D and 1/T (K^{-1}) was noted for all PAEs (Fig. S11). Thus, the activation enthalpy of diffusion was calculated from the slope of ln D versus 1/T using Eq. 4. The different diffusivities and/or mobilities of phthalates through PVC led to different enthalpies of diffusion. The enthalpy of diffusion was the highest for DIBP (194.4 $kJ \cdot mol^{-1}$) and the lowest for DNOP (127.4 $kJ \cdot mol^{-1}$).

Furthermore, the diffusivity of various phthalates in three commercially available PVC sheets was investigated. Contrary to the diffusion coefficients of mPVC at 40 °C, the diffusion coefficients of plasticizers present in all cPVCs (DEHT or DINP) were much higher (Table 2). At 40 °C, the diffusion coefficients of DINP in cPVC-1, cPVC-2, and cPVC-3 were $8.05 \pm 2.07 \times 10^{-11}$, $7.91 \pm 0.36 \times 10^{-10}$, and $9.22 \pm 0.17 \times 10^{-10}$ $cm^2 \cdot s^{-1}$, respectively, which were 3–4 orders of magnitude higher than the coefficients of DINP in mPVC ($6.70 \pm 3.17 \times 10^{-14}$). This difference may be attributed to PVC product type, thickness, initial total plasticizer concentration, and number of plasticizers added. Table S5 presents the migrated mass, migration ratio, and migration rates of plasticizers for all four types of PVCs. The dermal migration rate of DINP was dependent on the initial concentration of product, as cPVC-3 showed the highest values for migrated mass and migration rate. The diffusion coefficient of DEHP was greater in PVC with a higher initial DEHP fraction (Kim et al., 2003). The migration ratio of DINP was higher in all cPVCs than in mPVC, implying higher diffusion coefficients of DINP in cPVCs.

Furthermore, the extent of migration can be explained based on the results of EGA-MS. The total ion thermograms (TITs) of all PVC samples showed distinct temperature zones for plasticizer (phthalate) thermal desorption and PVC decomposition (Fig. 4). At lower temperatures, PVC decomposition results in the evolution of hydrogen chloride because of the lower dissociation energy between carbon and chlorine in the PVC structure. However, the residual hydrocarbon polymer is largely decomposed at temperatures between 100 °C and 550 °C. The average mass spectrum of each thermal zone on the TITs of PVCs showed plasticizers release at 149 m/z and HCl release at $m/z = 36$ and 38. The pyrolyzates of residual solid which decomposed on zone C were clearly indicates the thermal emission profiles. Although the decomposition temperatures of all PVCs were not significantly different, the evolution temperatures of plasticizers for mPVC and cPVCs were significantly different, likely related with different diffusion behaviors of plasticizers in the two types of PVCs. As shown in Fig. 4, the fraction of phthalate peak area to that of total organic chemicals (i.e., plasticizers, HCl from PVC, and PVC polymer itself) in all cPVCs was much greater than that in mPVC, resulting in a higher diffusivity of plasticizers in cPVCs. The total peak area for all plasticizers in mPVC was almost equivalent to the peak area of PVC, whereas the total peak area for all plasticizers in cPVCs was much higher than that of HCl and PVC itself. This result was further strengthened by the quantification of total chlorine content

Table 2
Calculated diffusion coefficient (D, $cm^2 \cdot s^{-1}$) and activation enthalpy of diffusion (H*, kJ mol^{-1}) for various plasticizers in modeled and commercial PVC (n = 4).

Plasticizer	Abbreviation	D (cm^2/s)			H* (kJ mol)
		25 °C	40 °C	60 °C	
Modeled PVC (mPVC)					
Dimethyl phthalate	DMP	$1.01 \pm 0.20 \times 10^{-13}$	$6.02 \pm 0.59 \times 10^{-12}$	$2.04 \pm 0.24 \times 10^{-10}$	178.9
Diethyl phthalate	DEP	$4.57 \pm 0.83 \times 10^{-14}$	$1.97 \pm 0.76 \times 10^{-12}$	$1.30 \pm 0.17 \times 10^{-10}$	187.5
Diisobutyl phthalate	DIBP	$1.20 \pm 0.25 \times 10^{-14}$	$3.43 \pm 1.82 \times 10^{-13}$	$4.39 \pm 0.27 \times 10^{-11}$	194.4
Dibutyl phthalate	DBP	$2.08 \pm 0.43 \times 10^{-14}$	$6.89 \pm 3.27 \times 10^{-13}$	$5.45 \pm 0.53 \times 10^{-11}$	186.0
Di-n-pentyl phthalate	DNPP	$1.81 \pm 0.11 \times 10^{-14}$	$3.38 \pm 1.81 \times 10^{-13}$	$2.17 \pm 0.30 \times 10^{-11}$	167.6
Benzyl butyl phthalate	BBP	$1.71 \pm 0.41 \times 10^{-14}$	$2.22 \pm 1.04 \times 10^{-13}$	$1.11 \pm 0.33 \times 10^{-11}$	153.0
Di(2-ethylhexyl) phthalate	DEHP	$5.55 \pm 0.40 \times 10^{-15}$	$8.15 \pm 6.33 \times 10^{-14}$	$6.01 \pm 1.90 \times 10^{-12}$	165.0
Dicyclohexyl phthalate	DCHP	$2.59 \pm 0.16 \times 10^{-15}$	$5.08 \pm 3.72 \times 10^{-14}$	$3.90 \pm 0.80 \times 10^{-12}$	159.1
Di-n-octyl phthalate	DNOP	$9.62 \pm 4.17 \times 10^{-15}$	$1.50 \pm 1.01 \times 10^{-13}$	$7.87 \pm 2.90 \times 10^{-12}$	127.4
Diisononyl phthalate	DINP	$2.07 \pm 0.21 \times 10^{-15}$	$6.70 \pm 3.17 \times 10^{-14}$	$4.34 \pm 1.23 \times 10^{-12}$	159.1
0.2–mm commercial PVC (cPVC–1)					
Di(2-ethylhexyl) terephthalate	DEHT	–	$1.05 \pm 0.30 \times 10^{-10}$	–	–
Diisononyl phthalate	DINP	–	$8.05 \pm 2.07 \times 10^{-11}$	–	–
0.3–mm commercial PVC (cPVC–2)					
Di(2-ethylhexyl) terephthalate	DEHT	–	$3.19 \pm 0.67 \times 10^{-10}$	–	–
Diisononyl phthalate	DINP	–	$7.91 \pm 0.36 \times 10^{-10}$	–	–
4.25–mm commercial PVC (cPVC–3)					
Diisononyl phthalate	DINP	–	$9.22 \pm 0.17 \times 10^{-10}$	–	–

of all PVC samples using CIC. When the plasticizers are added to the PVC, the mass fraction of vinyl chloride molecule in the plasticized PVC is decreased along with its chlorine content. It means that the Cl content is decreased with increase in mass of plasticizers in PVC. The chlorine content in mPVC (34.7 %) was higher than that in all cPVCs (26.3–31.5 %) (Table S6). The lower chlorine content of cPVC samples revealed that the plasticizer content of cPVCs was higher than that of mPVC, resulting in a higher diffusivity of plasticizers in cPVCs.

Moreover, TD-GC/MS results obtained after injecting the same amount of PVC sample suggested that the total concentration of plasticizers in cPVCs was relatively higher than that in mPVC, although mPVC showed a higher number of PAEs (10 types) than cPVCs (Fig. S12). Notably, some plasticizers present in the cPVC samples were not quantified owing to the unavailability of their standard solutions. Interestingly, when in TD-GC/MS results of mPVC, the peak intensities of all PAEs were lower than the HCl peak intensity. However, the peak intensities of unidentified plasticizers in cPVC were very high, while the intensities of other PVC components were low. The higher total plasticizer content of cPVCs suggests that these PVCs are much softer, more flexible, and less brittle (Marcilla et al., 2008; Marcilla et al., 2004) than mPVC, rendering their diffusion/migrate easier and faster.

Furthermore, this phenomenon can be explained on the basis of the free volume theory, as diffusivity also depends on free volume. The free volume or space within the polymer increases with increasing plasticizer content, which increases the migration of molecules (Czogała et al., 2021). With increase in the plasticizer content of polymers, the glass transition temperature is reduced, which increases the free volume of the polymer and ultimately the diffusivity of the plasticizers (Aziz et al., 2018; Joubert et al., 2002; Mauritz et al., 1990; Tsai and Chiu, 2022; Wei et al., 2019). In addition, plasticizers act as molecular lubricants, reducing the intermolecular friction between molecules (Langer et al., 2020). In addition, the greater degree of interaction of PAE molecules with the polymeric chains of mPVC and their higher steric hindrance may render the migration of PAEs difficult in the mPVC structure, because 10 types of PAEs (with some branched PAEs) were spiked in the tested mPVC (Coltro et al., 2014; Marcilla et al., 2004). Furthermore, the diffusion coefficients for compounds vary with the products and medium in which the migration test is performed.

Next, diffusion coefficients were compared with previous reports on various plasticizers present in PVC products (Table S7) (Clausen et al., 2015; Kim et al., 2003; Li et al., 2016; Ouchi et al., 2019; Takehisa et al., 2005; Tüzüm Demir and Ulutan, 2013; Yuan et al., 2020). The diffusion coefficients of different phthalates (DEP, DBP, DIBP, and BBP) obtained in the present study were similar to those for isooctane but relatively smaller than those for n-hexane and 95 % ethanol, as reported by Yuan et al. (Yuan et al., 2020). The diffusivity of DINP noted in the present study was comparable to that reported by Demir and Ulutan (Tüzüm Demir and Ulutan, 2013). In addition, the crystallinity of plastic products affects the diffusion coefficients of compounds present in them. Welle et al. (Welle and Franz, 2012) reported that poly(ethylene terephthalate) (PET) with higher crystallinity showed lower diffusion coefficients than amorphous PET. Although the temperature dependence of diffusion coefficients has been extensively studied, other factors that affect the diffusivity of plasticizers in plastic products are uncertain; thus, further studies are warranted to explore the effects of various parameters.

3.3. Association between diffusion coefficients and physicochemical properties of phthalates

The association between the diffusion coefficients of various PAEs in mPVC and their physicochemical properties were investigated. In general, the diffusion coefficients of phthalates decreased with increasing molar mass (Fig. 5). A similar trend was reported for various compounds when diffusion coefficients were plotted against molecular weights (Welle and Franz, 2012). The linear regression lines were plotted for ln D versus molecular weight (MW), and the correlations between the diffusion coefficient and molecular weight at different temperatures were obtained, as shown in Eqs. (6)–(8):

$$\ln D\ (\text{at } 25^{\circ}C) = -0.0180 \times MW - 19.003\ \left(R^2 = 0.8506\right) \quad (6)$$

$$\ln D\ (\text{at } 40^{\circ}C) = -0.0193 \times MW - 22.860\ \left(R^2 = 0.8091\right) \quad (7)$$

$$\ln D\ (\text{at } 60^{\circ}C) = -0.0091 \times MW - 28.933\ \left(R^2 = 0.4291\right) \quad (8)$$

At all temperatures tested, ln D showed a decreasing trend with increasing molecular weight of PAEs. A good linear relationship was observed between diffusivity and molecular weight at lower temperatures (25 °C and 40 °C); however, the linear relationship slightly deviated at higher temperatures (60 °C). This deviation was mainly due to the diffusion coefficients for DCHP and DINP, which were not close to the linear regression line, whereas coefficients for the other PAEs were close to the regression line. The slopes of curves were found to be similar at 25 °C and 40 °C, while those at 60 °C was approximately two times lower. The value of constant in linearized equation decreased with increasing temperature, resulting in

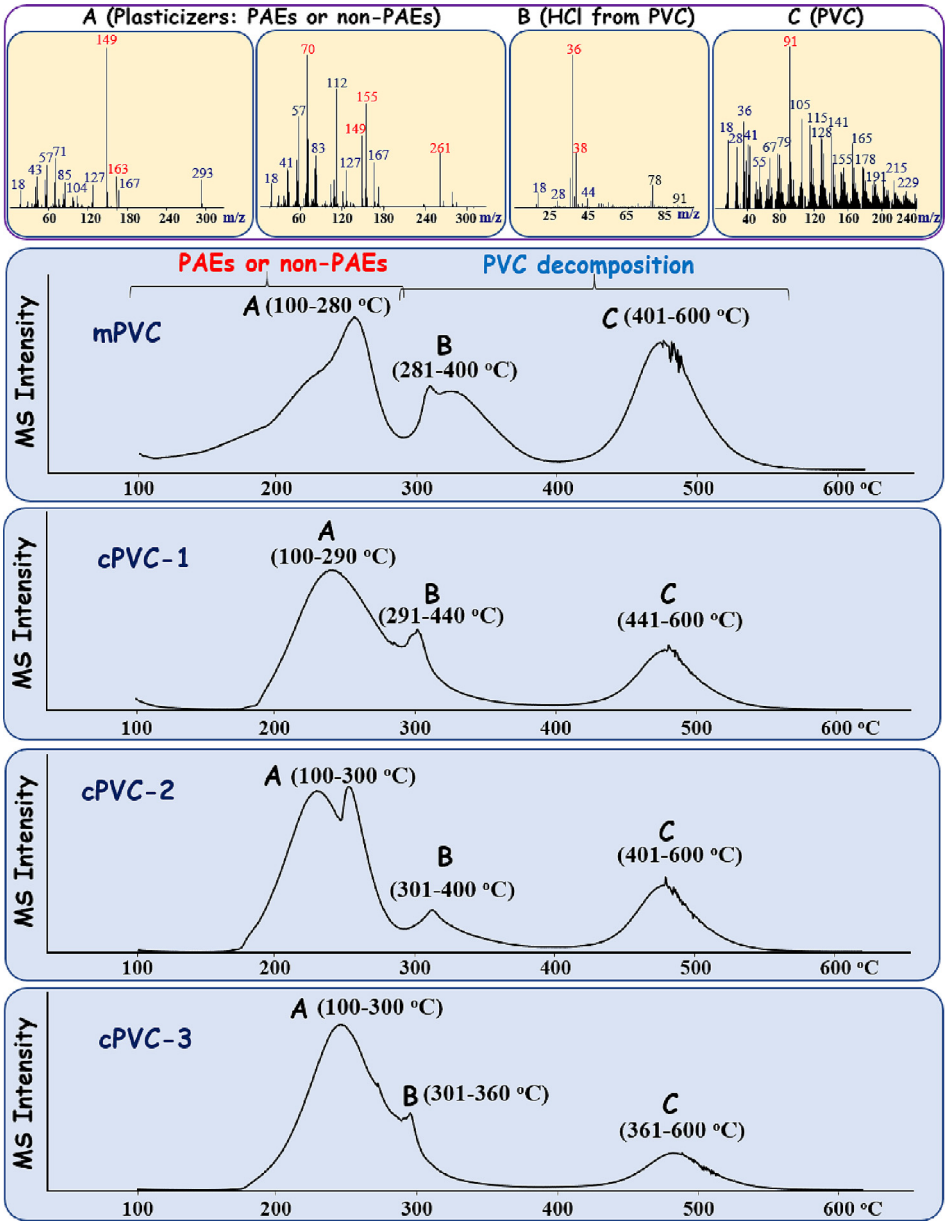


Fig. 4. Evolved gas analysis coupled to mass spectrometry total ion thermograms (TIT) of modeled polyvinyl chloride (mPVC) and three commercial PVCs (cPVCs). In all TITs, A, B, and C represent the peaks for plasticizers, HCl from PVC, and PVC itself, respectively. The Figures presented in the top are major peaks for PVC constituents at their respective *m/z* ratio.

an increase in diffusion coefficient. Therefore, the diffusion of PAEs depends on the molecular weights of compounds and temperature.

Overall, the diffusivity of PAEs decreased with increase in octanol–water partition coefficient (Fig. S13). However, a reverse trend was observed when lnD was plotted against vapor pressure and solubility, that is, diffusion coefficients increased with increase in vapor pressure, water solubility of PAEs, and aqueous diffusion coefficient (D_w). However, no linear relationship was detected among diffusion coefficient, density, and boiling point. In addition, as in the case of diffusion coefficients, the enthalpy of diffusion showed a similar trend when plotted (H*, kJ·mol^{-1}) against various parameters of PAEs (Fig. S14).

3.4. Environmental implication and future research

The mass of PAEs migrating from mPVC increased with time; however, the migration rate decreased with increasing time, which may decrease the dermal absorption rate of PAEs. The daily exposure dose (DED) was decreased with time; thus, the time weighted average DED was estimated for comparison (Fig. 6). The experimental temperature of 60 °C was used by considering an extremely harsh condition. At all temperatures, the DED was the highest for DMP, followed by DEP, and it generally decreased with increasing molar mass of PAEs (the lowest for DCHP). In addition, the DED of different PAEs increased by 3–9 and 8–39 times with increase in temperature from 25 °C to 40 °C and 60 °C, respectively. Therefore, the risk of dermal exposure to phthalates from PVC may be higher when PVC products are subjected to heat but lower at ambient room temperature. It should be noted that the daily exposure to DEHP, a widely used PAE at 0, 1, 2, and 4 mg/cm^2 sebum mass (at 25 °C) was found to be 0.012, 0.032, 0.043, and 0.067 μg kg^{-1} d^{-1}, respectively. In addition, the potential dermal exposure to plasticizer from cPVCs is directly proportional to the initial plasticizer content in PVC. The DED (at 40 °C) for DEHT was estimated at 3.5 (cPVC–1) and 133.6 μg kg^{-1} d^{-1} (cPVC–2) and that for DINP was found as 114.3, 0.6, and 430.5 μg kg^{-1} d^{-1} from cPVC–1, cPVC–2 and cPVC–3, respectively (Table S5).

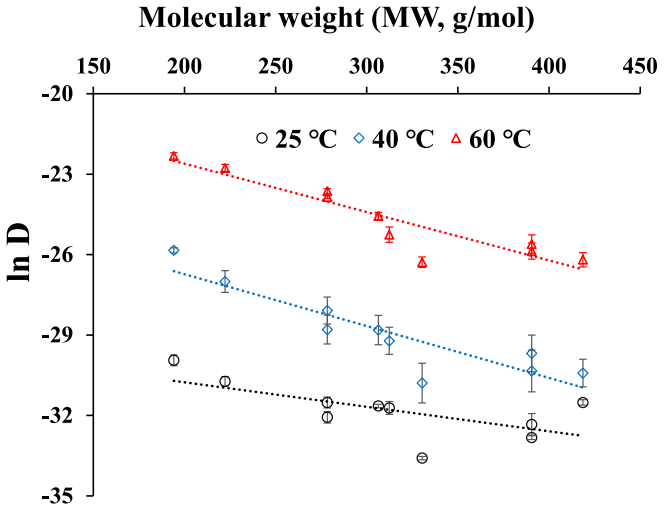


Fig. 5. Correlation between natural logarithm of the experimental diffusion coefficient (lnD) of different phthalic acid esters (PAEs) versus molecular weight (MW). Dashed lines indicate the best fit regression model and error bars represent the standard deviation of three replicates (n = 3). The equations for regression lines obtained are as follows: at 25 °C, lnD = −0.018 × MW − 19.0 (R^2 = 0.85); at 40 °C, lnD = −0.019 × MW − 22.9 (R^2 = 0.81); at 60 °C, lnD = −0.009 × MW − 28.9 (R^2 = 0.43).

The dermally absorbed dose for DEHP in aqueous solution using excised human viable skin permeation method is estimated to be 0.15–28.5 μg kg^{-1} d^{-1} (Hopf et al., 2014). A study estimated daily intake of plasticizers from indoor dust via dermal uptake, and found that dermal uptake of total phthalate and total non-phthalate plasticizers by adults is in the range of 0.0008–0.0017, and 0.0004–0.001 μg kg^{-1} d^{-1}, respectively (Subedi et al., 2017). In contrast, Gong et al. (2016) reported the dermally absorbed doses of DBP, DIBP, and DEHP for adults including or excluding body locations covered by cloth are in the range of about 500–2000 and 200–1200 μg kg^{-1} d^{-1} in summer and winter, respectively. Furthermore, the dermal exposure assessment for phthalates in skin wipes collected from human samples found the mean total dermal exposure in the range of 0.13–8.3 μg kg^{-1} d^{-1} (Zhao et al., 2022). Feng et al. (2020) reported the DED for total PAEs in indoor air in the range of 0.02–2.0 and 0.2–2.1 μg kg^{-1} d^{-1} for male and female, respectively. The daily dermal exposure dose to different phthalates for adult females in cosmetic and personal care products are ranged from 0.03 to 78 μg kg^{-1} d^{-1} (Koniecki et al., 2011). The DED of present study are found to be within the wide range of the existing literature data. Thus, the dermal exposure to plasticizers may vary with the different exposure scenario, suggesting that the dermal exposure assessment is required at different real environmental conditions.

The results of the present study can be used to predict the potential risk of human dermal exposure to plasticizers in consumer household products. Further study will be needed for percutaneous penetration of plasticizers in-vivo or in-vitro, along with various factors affecting dermal penetration, since it is reported that sebum does not enhance the dermal penetration of solvents (Schneider et al., 2016). In the future, the transfer of plasticizers from various consumer products to the human skin via sebum and/or sweat should be investigated along with the effect of pressure on dermal exposure to plasticizers to clarify these effects. In addition, the fate of plasticizers on the skin surface and the effects of periodic washing or showering on dermal intake should be explored. Moreover, the effect of the number of plasticizers added to PVCs, the chemical structure of plasticizers on migration and the interaction between different plasticizers in a product should be investigated. It is reported that mixtures of phthalate esters with one another exhibit cumulative, mainly dose-additive effects on the development of male reproductive tract when administered during sexual differentiation in utero (Howdeshell et al., 2008), suggesting a cumulative risk assessment for plasticizers via human biomonitoring (Wittassek et al., 2011). Lower–molecular weight PAEs (LPAEs) are usually used in personal care products, pesticides, lubricants, and paint solvents, whereas higher–molecular weight PAEs (HPAEs) are widely used in PVC and food packaging materials (Bajagain et al., 2023; Berger et al., 2018; Runkel et al., 2022). As the LPAEs have been replacing by higher HPAEs or other alternative plasticizers (APs) such as terephthalates, adipates, benzoate esters, citrates, trimellitates in recent years (LCSP, 2011; Nehring et al., 2020; Qadeer et al., 2022; Vieira et al., 2011; Wang and Qian, 2021), however, the consumption of PAEs is expected to remain high in the future (Hu et al., 2021). Since the APs are also not chemically bound to polymers, they can leach out from the products even at low diffusion or desorption rate, leading to health and ecological risks at their higher levels (Qadeer et al., 2022; Subedi et al., 2017). Thus, the migration and exposure to such plasticizers in different environment via various routes should also be considered.

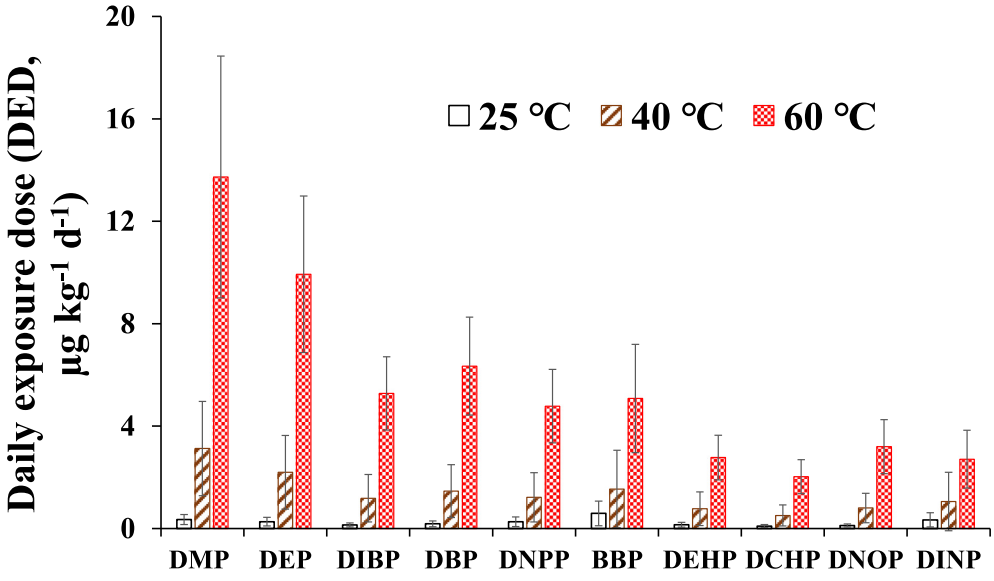


Fig. 6. Estimated daily exposure dose (DED) of different phthalic acid esters (PAEs) from modeled polyvinyl chloride (mPVC) at different temperature. Note that the temperature of 60 °C is used to estimate DED at extremely harsh condition.

4. Conclusions

In this study, the migration of plasticizers (phthalates/non-phthalates) from mPVC and cPVC products to PDMS via artificial sebum was investigated. The migrated mass, migration ratio, and migration rate varied across different products and compounds. Moreover, the effects of various environmental parameters on the dermal migration of phthalates from mPVC were investigated. The migration of all PAEs in mPVC increased with contact time, sebum mass, and temperature but decreased under pressure tested in the present study. Furthermore, PAEs with a low molecular weight migrated faster than those with a high molecular weight. The diffusion coefficients and activation enthalpies of diffusion for different PAEs were calculated, and the results were compared. The association between the diffusion coefficients and physicochemical properties of PAEs; such as molar mass, chemical structure, octanol–water partition coefficient, vapor pressure, water solubility, and aqueous diffusion coefficient; was explored. As such, DCHP showed the lowest migration results, which have two cyclohexane groups in the carbon chain. The DED of plasticizers from all PVCs was also evaluated for adults. In the future, exposure to phthalates via inhalation and ingestion routes and their toxicity should be assessed.

CRediT authorship contribution statement

Rishikesh Bajagain: Conceptualization, Methodology, Formal analysis, Data curation, Investigation, Writing – original draft, Visualization; **Gayatri Panthi:** Methodology, Investigation, Data curation; **Joung-Ho Park**: Methodology; **Jae-Kyoung Moon**: Methodology, Visualization; **Jihye Kwon**: Formal Analysis, Data curation; **Du Yung Kim**: Methodology, Investigation; **Jung-Hwan Kwon**: Writing - review & editing; **Yongseok Hong**: Conceptualization, Writing - review & editing, Supervision; Validation; Funding acquisition, Project administration; Resources. All authors have approved the final article.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.162412.

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