Malaysian Journal of Chemical Engineering & Technology 6(1) (2023) 1–8

Malaysian Journal of Chemical Engineering & Technology

Journal Homepage: http://myjms.mohe.gov.my/index.php/mjcet

e-ISSN: 2682-8588

A review on the assessment of plasticiser leaching from polyvinyl chloride and its prevention methods

Siti Nor Din *, Aula Aqila Yusrizal, Dalina Samsudin, Faiezah Hashim

Faculty of Applied Sciences, Universiti Teknologi MARA, Cawangan Perlis, Kampus Arau, 02600 Arau, Perlis, Malaysia

*Corresponding email: sitinor432@uitm.edu.my

Abstract

The production of the polyvinyl chloride (PVC) products is growing worldwide due to its high versatility and relatively low cost. However, PVC requires for plasticiser in order to improve its workability and flexibility to suit many applications area. The incorporation of plasticisers nevertheless comes with principle disadvantage which is the leaching out of the plasticisers used. Therefore, this review presents an overview of the leaching behaviour of plasticisers particularly for phthalate and natural-based plasticisers. Due to the problems that arise when leaching of plasticiser occurs, several methods to study the plasticiser leaching was elaborated which are Fourier transform infrared spectroscopy (FTIR), gas chromatography (GC), differential scanning calorimetric analysis (DSC), and migration stability test method. The results indicated that the leaching of the plasticisers could be identified by considering the loss of infrared characteristic band of plasticiser in the sample, retention time (t_R) level, glass transition temperature (T_g) level and weight change when using the methods mentioned above, respectively. Moreover, two widely used surface treatment methods to prevent plasticiser leaching which are plasma treatment and ultraviolet (UV) irradiation are also being provided. However, these two methods cannot fully suppress the migration of plasticiser especially plasticiser having a lower molecular weight as it is highly volatile and difficult to control. Therefore, there is a need for more crucial studies in designing the best treatment method for the bright future of zero migration of plasticisers to enhance the use of PVC applications.

Article Info

https://doi.org/10.24191/mjcet.v6i1.19737

Article history:

Received date: 14 September 2022
Accepted date: 10 April 2023
Published date: 30 April 2023

Keywords:

Phthalate
Polyvinyl chloride
Natural based plasticiser
Plasticiser leaching
Migration

1.0 Introduction

PVC is the second most commonly used plastic in the world after polyethylene, that has been widely used for various applications such as pipes and tubing, construction materials, packaging, electrical wiring and healthcare applications. Many researchers found that there is no material that could take over the specialty offered by PVC and even if there are some, the materials are neither as efficient nor economic as PVC (Ansar & Malvi, 2016). PVC is commercially available in either flexible or rigid form. However, the rigid properties of PVC are less favoured among the manufacturers thus need for an improvement in order to fit many applications that required for flexibility and stability properties.

Among the various types of additives, plasticisers are by far the most important ingredients for a PVC compound. Plasticiser is a small molecule incorporated into the polymeric materials to enhance flexibility, stability, workability, and dispensability of the polymer matrix (Bialecka-Florjańczyk & Florjańczyk, 2007). The reduction in T_g therefore giving a PVC softness and elastomeric characteristics.

Phthalates contributes to the largest group of PVC plasticisers having more than 80% of the total production (Yang et al., 2017). Phthalates provide an excellent plasticizing effect due to its good flexibility properties, good permanence and relatively low in cost (Marcilla et al., 2004).

However, several studies showed that phthalate-based plasticisers are problematic due to their toxic effect on humans and environments (Kumar, 2019). The relatively low molecular weight of this type of plasticisers enhancing the migration of the plasticiser from the PVC matrix such as by leaching and evaporation (Kumar, 2019), volatilization into the air, abrasion of the polymer, and direct diffusion from the polymer into dust on the polymer surface may cause adverse health effect to the human exposure (Eljezi et al., 2019).

This is happening because phthalates are not strongly and chemically bonded to the polymer matrix (Czernych et al., 2017). Instead, they are inserted mechanically between the PVC molecules, enabling the chains to slide pass each other giving PVC a flexibility. However, when the molecules do not combine chemically, the migration of the plasticiser out from the PVC matrix will occur causing toxic effects to the environment and human health. Therefore, these chemicals were believed to decrease these years by substitution of other alternative plasticisers (Pedersen et al., 2008).

The use of natural-based plasticisers which is a renewable source and non-harmful has been a relevant idea to replace phthalates. Natural-based plasticiser is becoming more popular these days due to its effectiveness and low costs (Vieira et al., 2011). Moreover, by using natural-based plasticiser, this could help in discarding the waste thus decreasing the environmental pollution as it is biodegradable. However, this class of plasticisers also have a common problem which is the migration of the plasticiser out from polymer. Even though its migration does not give the toxicity effect to the human health and environment, however it may result with the decrease in properties of the products.

Therefore, the permanence of plasticiser is one of the most important characteristics that need to be considered as it may lead to some problems during applications. Thus, in paper, the overall migration behaviour of phthalates and natural-based plasticisers towards PVC will be reviewed. Moreover, the recent methods to study the plasticiser leaching will also be elaborated. As the migration of the plasticisers is increasingly concerned, thus method to prevent the leaching of plasticisers will be discussed more in this paper to make it become a significant value to the plasticiser and PVC research community.

2.0 Types of plasticisers

2.1 Phathalate based plasticiser

There are many types of phthalate plasticisers that available commercially. Among them are di(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), dioctyl phthalate (DOP), dioctyl terephthalate (DOTP), diisononyl phthalate (DINP), diisodecyl phthalate (DIDP) and di-n-octyl phthalate (DnOP), and their general structure is given in Fig. 1.

Over the past few years, the toxicological impact of phthalate plasticisers raising a concern to the world. In 1998, the European Union suggested different guidelines value for amount of phthalate in toys (Marcilla et al., 2004). Later on, in 2005, the use of most common phthalate which are DEHP, DBP and BBP were eventually banned in European community in application for toys and childcare article while for DINP, DIDP and DnOP in applications intended for children which can be put in the mouth (Yang et al., 2010; U. S. EPA, 2013). The banning on the phthalates

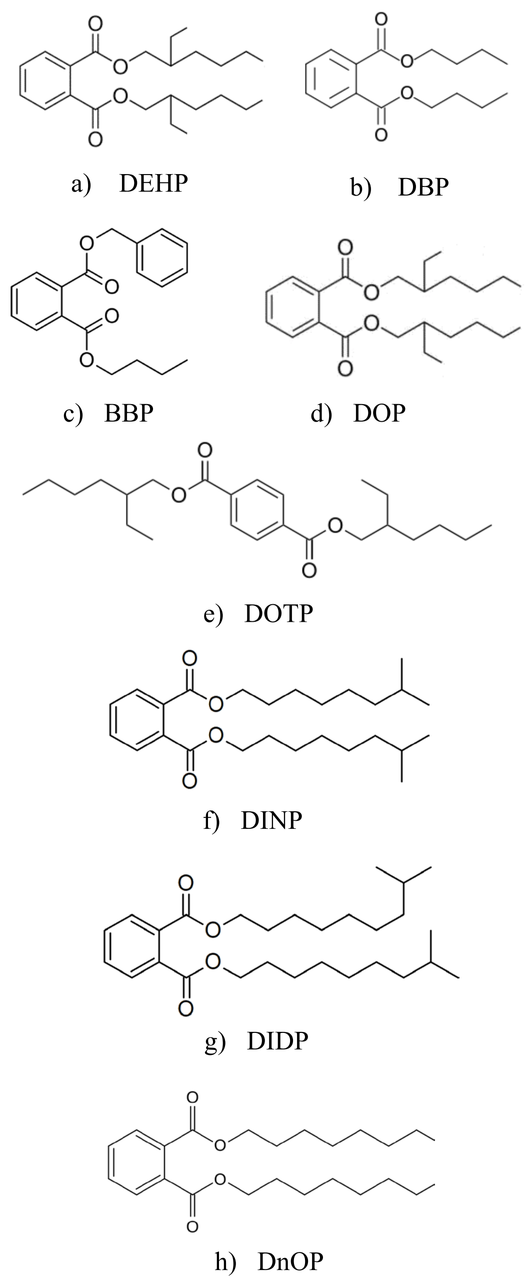


Fig. 1: Chemical structures of commonly used phthalate plasticisers (Wypych, 2012)

plasticisers indicate the importance of continued research in analysing the behaviour of the phthalates when being used in order to find the suitable replacement for this common plasticiser and find ways to suppress its migration phenomenon.

2.2 Natural-based plasticiser

Some type of natural-based plasticisers includes epoxidised soybean oil (ESBO) (Karmalm, 2009), palm oil-based derivatives such as palm oil-based alkyd (Lim et al., 2015), epoxidised linseed oil (ELO) (Fenollar et al., 2012) and castor oil (Chu & Ma, 2018). The chemical structure of the mentioned plasticisers is shown in Fig. 2.

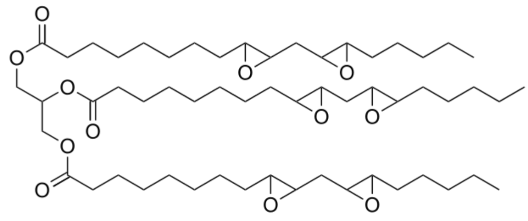
These natural based plasticisers are not sensitive to migration and toxicity therefore suitable for applications such as wire and cable, food packaging and children toys (Brostow et al., 2018).

3.0 Plasticiser leaching assessment methods

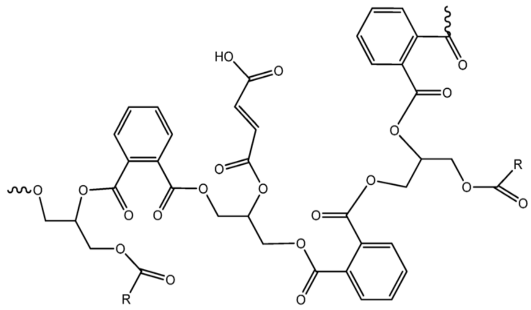
3.1 Fourier transform infrared spectroscopy (FTIR)

FTIR is the most popular method used in polymer study to determine the components existed in the material. Almost all research relies upon the use of FTIR in order to detect the specific migration of additives mainly plasticisers in the material. The FTIR operates by exposing the plasticised PVC sample to the infrared radiation (IR). Then, the bonds between different elements in the material will absorb the light at different frequencies. The absorbed light is measured by infrared spectrometer resulting in an output called infrared spectrum. By using FTIR, the components existed in the sample could be determined. In order to identify the migration of the plasticiser, the FTIR must be done before and after exposing the plasticised PVC to any migration stability test or various type of environments. From the results, the data obtained before and after can be characterised to observe the migration of the plasticiser.

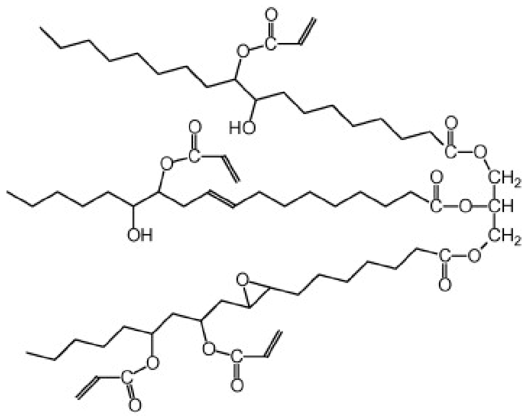
The infrared spectra usually attained characteristic bands of PVC at 715–556 cm^{-1} for C–Cl bonds and 1444–1414 cm^{-1} for C–H bonds. While for the plasticiser, the bands at 1477–1444 cm^{-1} usually attributed to the methyl ($–CH_3$) and 1803–1655 cm^{-1} to carbonyl group, as shown in Fig. 3 (Marcilla et al., 2008). Haishima et al. (2013) have used FTIR in analysing the surface structure of the PVC sheets with and without UV irradiation treatment in order to observe the migration of DEHP. From the result obtained, the carbonyl group of DEHP was found at



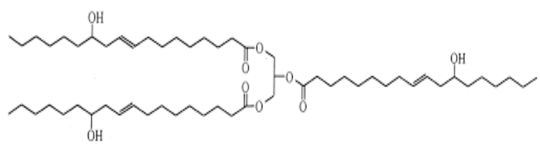
a) ESBO (Karmalm, 2009)



b) Palm oil-based alkyd (Lim et al., 2015)



c) ELO (Fenollar et al., 2012)



d) Castor oil (Chu & Ma, 2018)

Fig. 2: Chemical structures of natural-based plasticisers

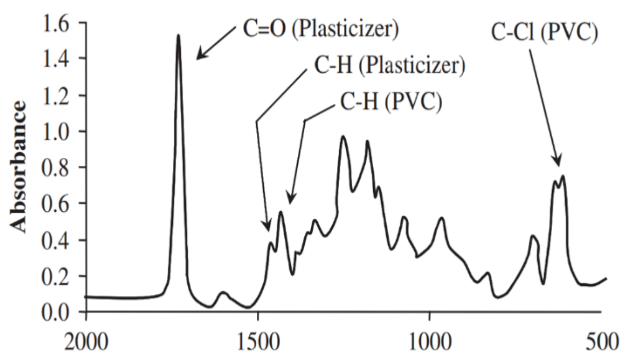


Fig. 3: Example of FTIR spectrum of PVC and plasticiser. (Marcilla et al., 2008)

1720 cm^{-1} and the alkane C–H bond of DEHP at 1250 cm^{-1}. When PVC was treated with UV irradiation, the result showed different broadened absorption bands while for non-irradiated sheet, the FTIR spectrum showed an identical result to the control PVC sheet, demonstrating that there were no changes of surface structure. This clearly indicates how FTIR works in identifying the leaching of plasticiser of one sample as it can detect the characteristic band of DEHP.

In the study reported by Belhaneche-Bensemra et al. (2002), on the migration of DEHP from plasticised PVC by using different analytical method including FTIR elaborated more clearly on how leaching of DEHP could be determined by using FTIR. From the findings, the PVC films spectra evidenced the migration of DEHP in sunflower oil. This is due to the progressive decrease of the DEHP bands after 9 days of testing, which can be seen from Fig. 4 below.

3.2 Gas chromatography (GC)

Apart from FTIR, another method that can be used to evaluate the plasticiser leaching is by using GC. GC is widely chosen because it is highly specific and commonly available (Earls et al., 2003). As plasticisers usually having a lower molar mass thus easily to vaporise, GC is suitable to be used as an analytical method in order to separate and analyse the sample as thermal decomposition will not take place. Many studies used GC or sometimes the combination of gas chromatograph-mass spectroscopy (GC-MS) in determining the plasticiser leaching phenomenon (Earls et al., 2003; Bueno-Ferrer et al., 2010; Hakkarainen, 2008). The result from GC spectrum should fulfil with two criteria which are the peaks of expected t_R can be found from the chromatogram and acceptable peak symmetry with minimal tailing (Earls et al., 2003).

GC was used in a study of determining the migration of phthalates plasticisers which are DEHP, DINP and DIDP from PVC toys applications that are intended or likely to be mouthed (Earls et al., 2003). The level of the migration of these phthalates were observed by the t_R which is the time taken for the individual component to elute from the column. The higher the t_R indicates the more time it takes to migrate out. From the result obtained, it showed that the trends of t_R increases from DEHP (23.48 min), DINP (24.0–26.5 min) and DIDP (25.0–27.5 min) clarifying that DEHP having the higher tendency to migrate out from PVC followed by DINP and lastly DIDP.

3.3 Differential scanning calorimetry (DSC)

DSC analysis can also be employed in order to detect the leaching of plasticisers. It is known that the incorporation of plasticiser into PVC will eventually lowering down the T_g level. After exposing the plasticised PVC to different experimental conditions, the migration can be identified when the T_g of the compound increased from the initial level demonstrating the compound losing its plasticisers and becomes brittle again. For that purpose, T_g of the compound can be acknowledged by the use of DSC and comparing it after being exposed to few conditions.

Belhaneche-Bensemra et al. (2002) used DSC in comparing T_g's of virgin PVC with T_g's of PVC with addition of DEHP. From Table 1 below, it can be clearly seen that the value of Tg decreases with increasing amount of DEHP. The 30% DEHP sample was then being exposed to sunflower oil for 10 days in order to evaluate the plasticiser migration. Consequently, the T_g value increases with the increase in exposure time as presented in Table 2. The T_g value at 10 days of exposing is close to the value of 10% DEHP displaying that the migration of DEHP occurred in the sample.

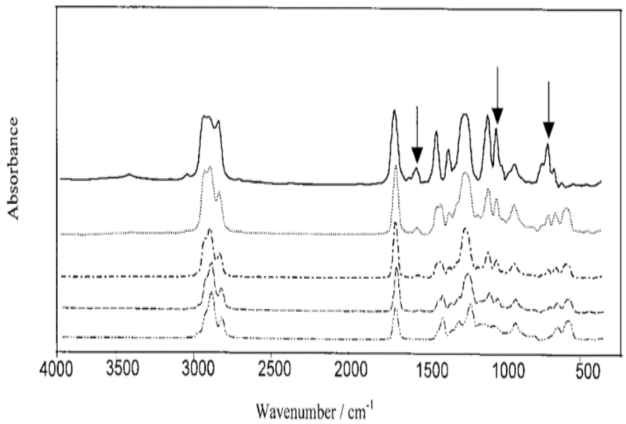


Fig. 4: FTIR spectra of DEHP/PVC films after submitted to the migration test with sunflower oil. From the highest line is the initial content of DEHP is 60%, followed by 0 day, 1 day, 5 days, and 9 days of exposure (Belhaneche-Bensemra et al., 2002)

Table 1: T_g for various formulations of PVC. (Belhaneche-Bensemra et al., 2002)

Sample	T_g (°C)
Virgin PVC	81.00
0% DEHP	69.40
10% DEHP	53.50
20% DEHP	33.30
30% DEHP	15.40

Table 2: T_g's values after different times of contact with sunflower oil. (Belhaneche-Bensemra et al., 2002)

Sample	T_g (°C)
0 days	15.40
4 days	26.20
10 days	48.50

3.4 Migration stability test

Migration stability test promotes the simplest method in detecting the leaching of the plasticisers from the PVC compounds. In migration stability test, the samples will be prepared by solvent casting method. Basically, all samples will be immersed into few different solvents typically water, ethanol, acetic acid and petroleum ether. After allotted period, the samples will be removed and weighed to calculate the mass loss in relation to the initial mass which is before being immersed. Due to the resistance of PVC to water, acid, alkali and almost all inorganic solvents and even hardly to dissolve in organic solvent, the weight loss of the PVC sample can be considered as the weight loss of plasticiser. The weight change can be simply calculated by using Eq. (1) shown below:

$$\text{Weight change} = \frac{(W - W_i)}{W_i} \times 100\% \tag{1}$$

where, W and Wi represent the current weight and the initial weight of a specimen, respectively.

An example of study that conducted this method is by Brostow et al. (2018) who mainly aim to differentiate the migration properties for hydrogenated castor oil and ESBO based plasticisers with conventional toxic plasticisers for PVC. The result showed that after 7 days all the weight of the samples highly increases except for the control sample. This indicates that the bio-based plasticisers used which are hydrogenated castor oil and ESBO do leached out from the compound. This phenomenon is believed to be occurring due to the lack of benzene ring which could prevent the migration from occurring as the rings are relatively large (Brostow et al., 2018).

Another research who also studied the migration of the plasticisers by the use of migration stability test was reported by Jia et al. (2017). The samples were immersed in four different types of solvent namely distilled water, 10% (v/v) ethanol, 30% (w/v) acetic acid and petroleum ether. From the result obtained, all samples showed no weight loss indicating that migration do not take place. The sample which is from phosphorus containing castor oil-based derivative acting as an internal plasticiser that is being covalently bonded to PVC-N3 showed zero migration as there is a strong interaction between the polymer chain and additive. The study conducted by Jia et al. (2017) who also studied the migration by leaching test of modified PVC (M-PVC) with DOP/PVC showed the same result in which no migration observed in M-PVC after being exposed to four different solvents which are also distilled water, 10% (v/v) ethanol, 30% (w/v) acetic acid and petroleum ether. While for DOP/PVC sample, the DOP was found to leach out in all solvents from the PVC blends. Next, the result from leaching test using deionised water worked by Lee et al. (2017) showed a reduced amount of weight loss of ESBO/PVC sample than that of DOP/PVC sample with 0.1% and 12.9% weight loss, respectively. This is mainly because the ESBO having a high molar mass compared to DOP, thus making it hardly to diffuse out. All of the above studies showed how migration stability test could be incorporated in examine the leaching of plasticisers in different solvents used.

4.0 Plasticiser leaching prevention methods

As discussed earlier, the incorporation of plasticisers into PVC or any polymer have a common problem which is the migration or leaching of the plasticiser out from the polymer matrix to its surrounding media during applications due to the thermodynamic reasons. This problem is gaining a huge concern as it will affect the end properties of the product and also impart serious health hazards as the plasticiser migrates to the surface contaminating physiological fluids in the body including blood, serum and plasma when PVC products are used for medical applications and child toys (Navarro et al., 2010). Therefore, several attempts have been developed in order to reduce or even suppress the leaching of the plasticiser from PVC.

The most common approaches that have been widely used among research in order to solve the migration problem is by surface modification. The main interactions that connect the plasticiser applied to the PVC take place at surfaces or interfaces. The interactions largely controlled by interplay of surface hydrophilicity, topography and chemical composition (Asadinezhad et al., 2012). The surface modification usually being applied to PVC as PVC is the main material and it also possesses few problems such as hydrophobicity, low surface energy, poor biocompatibility, unwanted protein adsorption and bacterial adhesion (Asadinezhad et al., 2012). To alleviate these problems, few types of surface modification have been applied in order to modify the surface properties and reducing the migration of the plasticiser out from PVC such as plasma treatment and UV irradiation. The crosslinking of the PVC surface as a result of chemical bonds between molecular chains can build a three-dimensional network structure on the PVC surface, then reduce the movement of the molecular chains and inhibit the migration of the plasticiser (Ma et al., 2020).

4.1 Plasma treatment

Plasma treatment is the most famous technique for surface modification. Plasma is defined as an active environment which contains a partially ionised gas such as free electrons, ions, radicals and neutral particles in which different interactions between energetic particles and the surface may take place (Asadinezhad et al., 2012). The natural problem possessed by PVC which is hydrophobicity as mentioned earlier leading to the difficulty in effective coating. Balazs et al. (2001) have investigated the possible surface modification by plasma treatment to PVC when used as medical devices in order to improve the antibacterial properties. The result showed that the plasma treatment does not induce any modification in the bulk polymer and yields an incorporation of an oxygenated functional group which will increase the surface wettability, giving a highly hydrophilic surface.

Another recent study by (Zhang et al., 2006) also reported a similar trend in which the oxygen plasma treatment process at relatively higher voltage than the traditional plasma treatment could form a hydrophilic surface on PVC permitting an effective coating of antibacterial reagents. Therefore, by using plasma treatment, the surface of the PVC can be modified in which it could form hydrophilic surface enabling in effective coating hence reducing the plasticiser migration.

Research by Zhang et al. (2013) have investigated the changes in molecular surface of PVC/dibutyl phthalate (DBP) and PVC/diethyl phthalate (DEP) films by oxygen and argon plasma treatment. From the sum frequency generation vibrational spectroscopy (SFG) result, DBP/PVC films showed larger DBP contribution on the surface while for DEP/PVC film, the film was dominated by PVC characteristic showing that DEP have leached out from the films. Zhang et al. (2013) believed that the leaching of DEP occurred by evaporation during pumping process due to its lower molecular weight resulting the molecule to be highly volatile in vacuum. While for DBP, the leaching of phthalate is not clear due to the disordering of surface groups and loss of elements such as chlorine, hydrogen, crosslinking chain scission since the induced energy exceeds the bond dissociation energy (Zhang et al., 2013; Asadinezhad et al., 2012). From here, we can conclude that plasma treatment does not disturb with the properties of the bulk polymer, however this treatment cannot fully inhibit the migration of plasticiser especially plasticiser having a lower molecular weight as it is highly volatile and difficult to control.

4.2 UV irradiation

UV irradiation is another one of the well-known psychochemical treatments applied to the polymer surfaces in order to alter the surface structures. This method has been studied by Haishima et al. (2013) in which it is aiming on supressing the migration of plasticisers in PVC medical devices. From the results, it was found that the sample being treated with strong UV intensity with a short period of time could suppress the migration of the DEHP thus preventing the toxicity effect. The reason why strong UV intensity could preferably prevent the leaching of plasticiser is due to the higher amount of UV intensity enhancing the formation of the crosslinked structure of the polymer (Haishima et al., 2013).

Ito et al. (2005) also reported the same trend, in which the application of UV irradiation on PVC products had decreased the levels of DEHP migration due to the changes in its surface structure. The oxidation and crosslinking reactions arise in the surface structure were detected by a decreased in C–Cl stretching vibration and the C–H band from the aromatic compound in PVC samples, hence reducing the plasticiser migration (Ito et al., 2005). Furthermore, this method can be easily performed under atmosphere without the needs of reagents or special instruments (Ito et al., 2005).

In another approach, Beveridge et al. (2018) chemically modified the surface properties of PVC materials, by altering the surface functionality through azidation reactions. It was found to be a practical approach for the surface derivatisation of commercial PVC tubing where the materials retained mechanical flexibility and translucency while preventing leaching of plasticiser (Beveridge et al., 2018).

5.0 Conclusions

The research on migration of plasticiser in PVC is a major concern in every PVC product due to the tendency of it to cause problems during applications. A brief discussion on migration phenomena is given along with a review, in the previous study. The topics mentioned in this review is focusing on how migration of plasticisers occurred when subjected to different experimental conditions and being discussed further in finding its reasons. Methods to study the leaching of plasticiser are also well documented and studied to understand how it works in identifying the migration that occurred. It is clearly showed that the leaching of the plasticisers could be identified by looking at the loss of characteristic band of plasticiser in the sample, t_R level, T_g level and weight change when using FTIR, GC, DSC and migration stability test method, respectively. Moreover, methods to prevent the plasticiser leaching are also provided and elaborated in order to find ways to suppress the migration ability of plasticisers out from PVC. In general, the migration of plasticisers from PVC needs to be studied more deeply in every PVC related product in order to make sure the migration occurred did not bring any disadvantages to the properties of the end products and do not harmful to the human health and environment. However, the high demand of PVC requires for more crucial studies on the migration level of every plasticiser used not only phthalate but also natural-based plasticisers. The provided migration level allowed for every plasticiser could be a reference for the use of plasticiser in the future therefore reducing the chance of problems that could arise when incorporating plasticiser in PVC products.

Authorship contribution statement

Siti Nor Din: Conceptualisation, Methodology, Writing – Review & Editing, Supervision. **Aula Aqila Yusrizal:** Investigation, Data curation, Writing- Original draft preparation. **Dalina Samsudin:** Methodology, Validation. **Faiezah Hashim:** Writing – Review & Editing.

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.

Acknowledgement

The authors would like to acknowledge the support of UiTM, Cawangan Perlis, Malaysia for providing the facilities and financial support on this research.

References

Ansar, K., & Malvi C. S. (2016). PVC Pipe Designer Furniture. *Journal of Polymer & Composites*, 4(2), 29–33.

Asadinezhad, A., Lehocký, M., Sáha, P., & Mozetič, M. (2012). Recent progress in surface modification of polyvinyl chloride. *Materials*, 5(12), 2937–2959. https://doi.org/10.3390/ma5122937

Balazs, D., Favez, D., Chevolot, Y., Xanthopoulos, N., Granges, C., Aronsson, B. O., Sidouni, F., Descouts, P. & Mathieu, H. J. (2001). Surface modification of PVC endotracheal tubes: Oxygen plasma treatment and aging effects. *Eur Cells Mater*, 1(Suppl 1), 18–24.

Belhaneche-Bensemra, N., Zeddam, C., & Ouahmed, S. (2002). Study of the migration of additives from plasticized PVC. *Macromolecular Symposia,* 180(1), 191–202. https://doi.org/10.1002/1521-3900(200203)180:1<191::AID-MASY191>3.0.CO;2-U

Beveridge, J. M., Chenot, H. M., Crich, A., Jacob, A., & Finn, M. G. (2018). Covalent Functionalization of Flexible Polyvinyl Chloride Tubing. *Langmuir*, 34(35), 10407–10412. https://doi.org/10.1021/acs.langmuir.7b03115

Bialecka-Florjańczyk, E., & Florjańczyk, Z. (2007). Solubility of plasticizers, polymers and environmental pollution. *Thermodynamics, Solubility and Environmental Issues*, 397–408. https://doi.org/10.1016/B978-044452707-3/50024-0

Bueno-Ferrer, C., Jiménez, A., & Garrigós, M. C. (2010). Migration analysis of epoxidized soybean oil and other plasticizers in commercial lids for food packaging by gas chromatography–mass spectrometry. *Food Additives and Contaminants*, 27(10), 1469–1477. https://doi.org/10.1080/19440049.2010.502129

Brostow, W., Lu, X., & Osmanson, A. T. (2018). Nontoxic bio-plasticizers for PVC as replacements for conventional toxic plasticizers. *Polymer Testing*, 69, 63–70. https://doi.org/10.1016/j.polymertesting.2018.03.007

Czernych, R., Chraniuk, M., Zagożdżon, P., & Wolska, L. (2017). Characterization of estrogenic and androgenic activity of phthalates by the XenoScreen YES/YAS in vitro assay. *Environmental Toxicology and Pharmacology*, 53, 95–104. https://doi.org/10.1016/j.etap.2017.05.010

Chu, H., & Ma, J. (2018). A strategy to prepare internally plasticized PVC using a castor oil-based derivative. *Korean Journal of Chemical Engineering*, 35(11), 2296–2302. https://doi.org/10.1007/s11814-018-0118-5

Earls, A. O., Axford, I. P., & Braybrook, J. H. (2003). Gas chromatography–mass spectrometry determination of the migration of phthalate plasticisers from polyvinyl chloride toys and childcare articles. *Journal of chromatography A*, 983(1–2), 237–246. https://doi.org/10.1016/S0021-9673(02)01736-3

Eljezi, T., Pinta, P., Nativel, F., Richard, D., Pinguet, J., Roy, O., Sautou, V., Grimandi, G. and Moreau, E. (2019). In vitro cytotoxic effects of secondary metabolites of DEHP and its alternative plasticizers DINCH and DINP on a L929 cell line. *International Journal of Hygiene and Environmental Health*, 222(3), 583–589. https://doi.org/10.1016/j.ijheh.2019.03.005

Fenollar, O., Garcia-Sanoguera, D., Sánchez-Nácher, L., López, J., & Balart, R. (2012). Characterization of the curing process of vinyl plastisols with epoxidized linseed oil as a natural-based plasticizer. *Journal of applied polymer science,* 124(3), 2550–2557. https://doi.org/10.1002/app.34645

Haishima, Y., Isama, K., Hasegawa, C., Yuba, T., & Matsuoka, A. (2013). A development and biological safety evaluation of novel PVC medical devices with surface structures modified by UV irradiation to suppress plasticizer migration. *Journal of Biomedical Materials Research Part A*, 101(9), 2630–2643. https://doi.org/10.1002/jbm.a.34558

Hakkarainen, M. (2008). Migration of monomeric and polymeric PVC plasticizers. *Advances in Polymer Science,* 211(1), 159–185. https://doi.org/10.1007/12_2008_140

Ito, R., Seshimo, F., Haishima, Y., Hasegawa, C., Isama, K., Yagami, T., Nakahashi, K., Yamazaki, H., Inoue, K., Yoshimura, Y., Saito, K., Tsuchiya, T., & Nakazawa, H. (2005). Reducing the migration of di-2-ethylhexyl phthalate from polyvinyl chloride medical devices. *International journal of pharmaceutics*, 303(1–2), 104–112. https://doi.org/10.1016/j.ijpharm.2005.07.009

Jia, P., Wang, R., Hu, L., Zhang, M., & Zhou, Y. (2017). Self-Plasticization of PVC via click reaction of a monooctyl phthalate derivative. *Polish Journal of Chemical Technology*, 19(3), 16–19. https://doi.org/10.1515/pjct-2017-0042

Karmalm, P., Hjertberg, T., Jansson, A., & Dahl, R. (2009). Thermal stability of poly (vinyl chloride) with epoxidised soybean oil as primary plasticizer. *Polymer Degradation and Stability,* 94(12), 2275–2281. https://doi.org/10.1016/j.polymdegradstab.2009.07.019

Kumar, S. (2019). Recent developments of biobased plasticizers and their effect on mechanical and thermal properties of poly (vinyl chloride): A review. *Industrial & Engineering Chemistry Research*, 58(27), 11659–11672. https://doi.org/10.1021/acs.iecr.9b02080

Lee, Sangjun, Yuk, Jeong-Suk, Kim, A-Ryeon, Choung, Ji Sun, Shin, Jihoon, & Kim, Young-Wun. (2017). Polyvinylchloride Plasticized with Acetylated Monoglycerides Derived from Plant Oil. *Applied Chemistry for Engineering,* 28(1), 42–49. https://doi.org/10.14478/ACE.2016.1099

Lim, K. M., Ching, Y. C., & Gan, S. N. (2015). Effect of palm oil bio-based plasticizer on the morphological, thermal and mechanical properties of poly (vinyl chloride). *Polymers,* 7(10), 2031–2043. https://doi.org/10.3390/polym7101498

Ma, Y., Liao, S., Li, Q., Guan, Q., Jia, P., & Zhou, Y. (2020). Physical and chemical modifications of poly (vinyl chloride) materials to prevent plasticizer migration - Still on the run. *Reactive and Functional Polymers*, 147, 104458. https://doi.org/10.1016/j.reactfunctpolym.2019.104458

Marcilla, A., García, S., & García-Quesada, J. C. (2004). Study of the migration of PVC plasticizers. Journal of *Analytical and Applied Pyrolysis*, 71(2), 457–463. https://doi.org/10.1016/S0165-2370(03)00131-1

Marcilla, A., Garcia, S., & Garcia-Quesada, J. C. (2008). Migrability of PVC plasticizers. *Polymer Testing*, 27(2), 221–233. https://doi.org/10.1016/j.polymertesting.2007.10.007

Navarro, R., Perrino, M. P., Tardajos, M. G., & Reinecke, H. (2010). Phthalate plasticizers covalently bound to PVC: Plasticization with suppressed migration. *Macromolecules*, 43(5), 2377–2381. https://doi.org/10.1021/ma902740t

Pedersen, G. A., Jensen, L. K., Fankhauser, A., Biedermann, S., Petersen, J. H., & Fabech, B. (2008). Migration of epoxidized soybean oil (ESBO) and phthalates from twist closures into food and enforcement of the overall migration limit. *Food additives & contaminants. Part A, Chemistry, analysis, control, exposure & risk assessment*, 25(4), 503–510. https://doi.org/10.1080/02652030701519088

U.S. EPA (2013). America's Children and the Environment (ACE). Third Edition. https://www.epa.gov/sites/default/files/2015-06/documents/ace3_2013.pdf

Vieira, M. G. A., da Silva, M. A., dos Santos, L. O., & Beppu, M. M. (2011). Natural-based plasticizers and biopolymer films: A review. *European Polymer Journal,* 47(3), 254–263. https://doi.org/10.1016/j.eurpolymj.2010.12.011

Wypych, G. (2012) Handbook of Plasticizers (2nd Edition). ChemTec Publishing, 7–83, https://doi.org/10.1016/B978-1-895198-50-8.50004-7.

Yang, Z., Peng, H., Wang, W., & Liu, T. (2010). Crystallization behavior of poly(εcaprolactone)/layered double hydroxide nanocomposites. *Journal of Applied Polymer Science*, 116(5), 2658–2667. https://doi.org/10.1002/app.31787

Yang, Y., Huang, J., Zhang, R., & Zhu, J. (2017). Designing bio-based plasticizers: Effect of alkyl chain length on plasticization properties of isosorbide diesters in PVC blends. *Materials and Design*, 126, 29–36. https://doi.org/10.1016/j.matdes.2017.04.005

Zhang, W., Chu, P. K., Ji, J., Zhang, Y., Liu, X., Fu, R. K. Y., Yan, Q. (2006). Plasma surface modification of poly vinyl chloride for improvement of antibacterial properties. *Biomaterials,* 27(1), 44–51. https://doi.org/10.1016/j.biomaterials.2005.05.067

Zhang, X., Zhang, C., Hankett, J. M., & Chen, Z. (2013). Molecular surface structural changes of plasticized PVC materials after plasma treatment. *Langmuir*, 29(12), 4008–4018. https://doi.org/10.1021/la4000796