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Circular economy without chemicals controls? Evidence of recirculated toxic plasticizers in flexible PVC products

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Abstract

The global push towards a circular economy (CE) has led to increasing efforts to improve resource utilization efficiency, including plastics recycling. However, the presence of additives, especially those that are toxic, complicates plastics recycling in several ways. Without sufficient controls, the spread of hazardous additives via recycling activities represents a significant public health challenge, particularly among developing nations. This study demonstrates evidence of such uncontrolled recycling, based on an investigation of four household flexible PVC product groups available in Thailand. A versatile pyrolysis/thermal desorption gas chromatography-mass spectrometry (Py/TD-GC-MS) method was employed to simultaneously screen 18 target plasticizers in these products. Di-(2-ethylhexyl) phthalate (DEHP) and diisononyl phthalate (DINP) are the most frequently detected primary plasticizers. DEHP is dominant in vinyl boots, flooring sheets, and hoses, while DINP is dominant in cable sheaths, likely due to a spill-over effect from the EU Restriction of Hazardous Substances (RoHS) directive. Chlorinated paraffins (CPs) are secondary plasticizers that are also detected in most samples, except for boots. The other plasticizers detected include other ortho-phthalates and non-phthalates. These results provide insight into combinatory patterns of plasticizer 'cocktails', that comprise restricted, as-yet-unrestricted, and non-restricted plasticizers, embedded in the same individual samples, with a maximum of seven plasticizers found in a single cable sheath. These findings indicate the existence of potentially risky recycling practices that target embedded plasticizers to save cost, without due consideration of their inherent toxicity. Proper interventions are necessary to ensure that CE and chemical safety can be synergized.

Keywords: PY/TD-GC-MS, toxic plasticizers, plasticizer recycling, chemicals in products, simultaneous screening, uncontrolled PVC recycling, circular economy, phthalates

INTRODUCTION

Plasticizers are chemical substances that are added to materials, especially polymers and rubbers, to lower their glass transition temperatures, to make them more flexible and easy to process[1]. There are two plasticization methods, namely internal and external[2]. In external plasticization, plasticizers are blended into base polymers without forming chemical bonds[3], such that subsequent exudation from the polymer matrices can occur[4]. As some external plasticizers are carcinogenic, mutagenic, or toxic to reproduction (CMRs), endocrine-disrupting, or persistent[5-8], their release during lifecycle stages has raised safety concerns.

Plasticizers are divided into two types, namely, primary and secondary. Primary plasticizers are the main substances that deliver the desired physical properties without incompatibility problems. There are several families of primary plasticizers, including ortho-phthalate esters [PAEs, such as DEHP, DINP, dibutyl phthalate (DBP), diisobutyl phthalate (DIBP), diisodecyl phthalate (DIDP), and benzyl butyl phthalate (BBP)], adipate esters [such as dioctyl adipate (DOA), di(2-ethylhexyl) adipate (DEHA), and diisononyl adipate (DINA)], benzoate esters [such as diethylene glycol dibenzoate (DEGDB), and isononyl benzoate (INB)], trimellitate esters [such as tris-2-ethylhexyl trimellitate (TOTM)], terephthalate esters (such as DEHT or DOTP), phosphate esters [such as tris(2-ethylhexyl) phosphate, TPP], citrate esters [such as acetyl tributyl citrate (ATBC), tributyl citrate (TBC), and triethyl citrate (TEC)], and cyclohexanoate esters (such as DINCH)[9]. Globally, approximately 8.4 million tonnes of plasticizers are produced annually, with most (~90%) used to produce flexible polyvinyl chloride (PVC) products, and PAEs being the most frequently used, followed by terephthalates and cyclohexanoates[10-12].

The amount of plasticizer required to soften PVC to achieve the desired flexibility depends on the chemical structure, molecular weight (MW), and functional groups, and can range from several percent for semi-rigid applications (such as curtains and shoe heels) to 40% for highly flexible applications (such as boots and gloves) and > 80% for extremely flexible applications (such as lures)[13]. Plasticizers with a lower MW and smaller number of polar groups provide higher flexibility at a given content[1].

In contrast, secondary plasticizers are used in addition to primary plasticizers to reduce cost and/or improve fire resistance[13]. These substances are less compatible with the base polymers and can exude out under normal conditions. Polychlorinated *n*-alkanes or chlorinated paraffins (CPs) constitute a key family of secondary plasticizers. CPs can be used with antimony trioxide to further improve fire protection performance. CPs are typically grouped into short-chain CPs (SCCPs, C_{10-13}), medium-chain CPs (MCCPs, C_{14-17}), and long-chain CPs (LCCPs, C_{18-30}). However, CPs produced in Asia (such as India and China) are instead supplied based on their chlorine content. Thus, they can contain broader ranges of carbon chain lengths. For example, CP-52, the most popular CP in China, contains C_{9-30} chain lengths, with chlorine contents of 40%-63% by weight[14]. Globally, the production volume of CPs is estimated at more than 1 million tonnes per year, with the production of MCCPs being much higher than that of SCCPs[15]. As much as 236.4 kilotons (kt) of SCCPs and 450.2 kt of MCCPs were used in China in 2019, mainly to produce PVC products[6].

Based on keywords searches from Thailand's Department of Industrial Works online factory database[16] and Office of Natural Resources and Environmental Policy and Planning's Environmental Impact Assessment (EIA) reports database[17], at least four registered factories produce primary plasticizers in Thailand. Among them are two large-sized factories producing PAEs and non-PAEs with combined capacities of about 80 kt/year for DEHP, DINP, and DPHP, and 6 kt/year for TOTM, DOA, and DEHT. The combined consumption of primary plasticizers in Thailand in 2010 was about 95 kt (based on private communication with a local plasticizer association), with DEHP consumption (47%) being slightly higher than DINP consumption (45%), while the consumption of other PAEs and non-PAE alternatives remained relatively low (4% for DIDP and < 5% for the rest). Most demand for DEHP and DINP (80%) was met by domestic production. Furthermore, two factories produce MCCPs, with undisclosed production capacities. The amounts of plasticizers consumed indirectly through imported products are currently unknown.

Previous studies have shown that various consumer plastic products (mostly PVC) contain PAEs as primary plasticizers. To date, most investigated applications have been related to toys and childcare items[18-24], followed by cosmetics/personal care products and medical devices[19,25-27]. Although it is common knowledge that SCCPs and MCCPs are used in PVC, the number of studies is limited[6,7,28-31]. Furthermore, the number of reports on patterns of PAEs and CPs blended in the same PVC items is very limited.

Seventeen PAEs have been included in the European Candidate list of Substances of Very High Concern (SVHCs) for authorization under the REACH Regulation[32]. Four low-molecular-weight (LMW) PAEs (BBP, DBP, DEHP, and DIBP) are prohibited under Annex XVII of the REACH Regulation for uses in any plasticized materials[33], and under the EU RoHS Directive for electrical and electronic equipment[34]. Three high-molecular-weight (HMW) PAEs (DnOP, DIDP, DINP) are also prohibited for use in toys and childcare items, which can be placed in children's mouths, under Annex XVII of the REACH Regulation[35].

Furthermore, SCCPs (C_{10} to C_{13} and with chlorine contents greater than 48% by weight) have been listed as Persistent Organic Pollutants (POPs) in Annex A of the Stockholm Convention (SC) in 2017[36] and in the EU POPs Regulation in 2019[37]. According to the SC, any CPs with SCCP contents greater than 1% are considered POPs[6]. These global restrictions have resulted in the transition from LMW PAEs to either HMW PAEs (such as DINP, DIDP, and DPHP) or non-phthalates (such as DEHT, TOTM, and DOA)[38], and from SCCPs to MCCPs[6,7,39]. However, in July 2021, MCCPs, a common replacement for SCCPs, were added to the EU Candidate List of SVHCs[32], and are currently being reviewed by the POPs Reviewing Committee for possible inclusion as SC POPs. In Thailand, DEHP and SCCPs are Category 3 controlled substances under the Hazardous Substances Act[40,41]. Any production, import, export, or possession of these substances requires prior approval from the Department of Industrial Works.

The leakage of plastic-born plasticizers of concern into the environment at various lifecycle stages has been widely reported, including from factories[42-44], storage and distribution[45], usage[46], and plastic recycling[47], and e-waste recycling[48,49], which could lead to exposure via inhalation, dermal absorption, and ingestion of soil/dust and contaminated crops[50]. Direct exposure to hazardous plasticizers embedded in plastic items used in daily life is of great concern owing to their relatively high concentrations, and proximity to users and long duration of contact. In regions with stringent regulatory controls, such as the EU, incidental retention and recirculation of restricted plasticizers in society still occur, and are partly attributed to CE-driven actions, such as extended use, reuse, and repurposing of affected 'old' plastic items[24], as well as materials recycling, causing the inadvertent spread of hazardous plasticizers[22,51]. By comparison, public exposure to these plasticizers of concerns in developing regions is expected to be more severe owing to deficient controls during the lifecycle of potentially affected plastic products.

As with other thermoplastics, PVC items, rigid or flexible, can be recycled. Furthermore, like most other additives, the embedded plasticizers are generally more expensive than their PVC matrices, making their recovery sought after. This is especially relevant for soft PVC items, in which the overall plasticizer content can exceed those of PVC resins. Elevated exposure risks are associated with naive practices in materials recycling, where inputs are selected for their price and functionality alone without due consideration of their inherent toxicity. Such end-of-life (EOL) plasticized PVC inputs are converted into 'new' PVC products, possibly with little or no additional plasticizers needed[52], resulting in resource and cost savings, but potentially also a multitude of 'new' affected products. Over the past decades, scrap shops in Thailand have been buying back EOL flexible PVC items at prices comparable to high-value plastic scraps, such as PET and HDPE bottles (see Supplementary Figure 1), which suggests that mechanical recycling of plasticized PVC has been a common practice. While this resource-saving practice might appear in line with CE principles, any benefits might not justify the potential magnification of exposure risks if the plasticizers in question are toxic. Such risky practices could be partly attributed to the economic and awareness levels of local entrepreneurs and consumers, and partly to the lack of action by responsible authorities.

In terms of plasticizer characterization, the increasing number of regulations enforced to control certain harmful plasticizers and flame retardants[32,34-36,53-56] creates a growing demand for rapid analysis methods to monitor toxic additives in the large and ever-increasing amount of products. Gas chromatography-mass spectrometry (GC-MS) using a pyrolyzer/thermal desorption accessory (Py/TD-GC-MS) has been proposed as an alternative technique to identify plasticizers in polymers, because plasticizers are typically more volatile[57] and can be thermally desorbed from polymer matrices without the need for complex and time- and resource-intensive solvent extraction procedures[18,58]. Py/TD-GC-MS has been validated and adopted by the International Electrotechnical Commission as a standard test method (IEC 62321-8: 2017) for the screening and semi-quantitative analysis of seven PAEs (BBP, DBP, DEHP, DIBP, DIDP, DINP, and DnOP) in polymers in the range of 100-2000 mg/kg[59]. Py/TD-GC-MS has been investigated in several studies for the identification and, in some cases, semi-quantification of other organic additives, including SCCPs and other flame retardants[60,61].

This study aimes to investigate the potential intermixing of 18 target plasticizers [Table 1] in four consumer product groups (vinyl flooring sheets, garden hoses, vinyl boots, and wire and cable sheaths), which were selected for their prevalence in Thailand. The 18 targeted plasticizers were selected based on a US Chronic Hazard Advisory Panel (CHAP) report of known uses[62]. The production of these flexible PVC products is known to utilize large amounts of plasticizers[13], and the resulting items can come into close contact with users. A total of 153 soft PVC samples were characterized using Py/TD-GC-MS to simultaneously screen for the target plasticizers. The results provide insight into the combinatory patterns of plasticizer 'cocktails', comprising restricted (LMW PAEs and SCCPs), as-yet-unrestricted (HMW PAEs and MCCPs), and non-restricted plasticizers (non-PAEs) embedded in the same individual samples. These findings confirm the existence of uncontrolled recycling practices that target the embedded plasticizers, at least for products available on the Thai market. To our knowledge, this is the first report on the uncontrolled mixing of diverse plasticizer types in the four selected groups of flexible PVC products. Note that this study intends to concurrently screen all targeted plasticizers to study their combinatory patterns in the samples, but not precisely quantify the individual substances.

Table 1. Target plasticizers in this work

Compound	Abbreviation	CAS	Limits ({Regulations*})
Benzyl butyl phthalate	BBP	85-68-7	Each < 0.1% by weight of plasticized material ({1}{2}{3}); Sum of (DBP, BBP, DIBP and DEHP) < 0.1% by weight of plasticized material ({4} Entry 51) Sum of (DBP, BBP and DEHP) in toys < 0.1% by weight ({5}) DEHP no limit specified ({6})
Dibutyl phthalate	DBP	84-74-2	
Diethylhexyl phthalate	DEHP	117-81-7	
Diisobutyl phthalate	DIBP	84-69-5	
Diisodecyl phthalate	DIDP	26761-40-0	Each < 0.1% by weight ({1}) Sum of (DnOP, DINP, and DIDP) < 0.1% by weight of plasticized material ({4} Entry 52) Sum of (DBP, BBP, DEHP, DINP, DIDP and DnOP) < 0.1% by weight for toys intended for children aged 3 and younger and children's toys that can be placed in a child's mouth ({5})
Diisononyl phthalate	DINP	28553-12-0# and 68515-48-0	
Di-n-Octyl phthalate	DnOP	117-84-0	
Short-chain chlorinated paraffins (C_{10-13})	SCCPs**	Various (e.g., 85535-84-8, 71011-12-6, 108171-26-2)	{7},{8} < 0.15% by weight {6} no limit specified
Medium-chain chlorinated paraffins (C_{14-17})	MCCPs**	Various (e.g., 85535-85-9, 198840-65-2, 1372804-76-6)	{3} < 0.1% by weight
Diallyl phthalate	DAP	131-17-9	
Dicyclohexyl phthalate	DCHP	84-61-7	
Di(2-ethylhexyl) terephthalate	DEHT	6422-86-2	
Diethyl phthalate	DEP	84-66-2	
Diheptyl phthalate	DHP	3648-21-3	
Diisononyl cyclohexane-1, 2-dicarboxylate	DINCH	166412-78-8	
Dimethyl phthalate	DMP	131-11-3	
Di(2-ethylhexyl) Adipate	DOA	103-23-1	
Dipentyl phthalate	DPP	131-18-0	
Tris(2-ethylhexyl) trimellitate	TOTM	3319-31-1	

Regulations* {1}: US CPSIA[54]; {2}: EU RoHS[34,53]; {3}: EU REACH SVHC Candidate list[32]; {4}: EU REACH Annex XVII[33], {5}: Thai Industrial Standard[63]; {6}: Category 3 substance under Thailand's Hazardous Substances Act; {7}: Stockholm Convention[36]; {8}: EU POPs Regulation[37].
**No rigorous distinction between SCCPs and MCCPs is made in this study.
#Only DINP with CAS No 28553-12-0 is included in this study.

EXPERIMENTAL

Reagents and Materials

Reference materials (DCHP, DEHP, DEHT, and DEP, ≥ 99.5% purity; DBP, DIBP, DINP, DMP, DOA, DPP, and TOTM, ≥ 99% purity; BBP and DnOP, ≥ 98% purity; DHP, ≥ 97% purity; and DAP and DIDP, ≥ 96.5% purity) were purchased from Sigma-Aldrich (USA). A commercial MCCP containing 52% Cl (≥ 97% purity), hereafter denoted as c-MCCP, was donated by a local producer. Standard reference solutions (six chlorinated paraffins solutions, 1000 g/mL in cyclohexane (SCCPs, C_{10-13}, with chlorine contents of 63%, 55.5%, and 51.5%; MCCPs, C_{14-17}, with chlorine contents of 57%, 52%, and 42%) and a mixture of 16 phthalate esters ('Phthalate Mixture 956') in isooctane, 1000 µg/mL) and internal/surrogate standards (gamma-HCH, 1000 g/mL in toluene; 4,4'-dibromooctafluorobiphenyl, 100 g/mL in cyclohexane; and decachlorobiphenyl, 100 g/mL in isooctane) were purchased from Dr. Ehrenstorfer/LGC (Germany). General-purpose, commercial-grade virgin PVC powder (k-value of 66 and apparent bulk density of 0.550 g/mL) was purchased from a local producer. All solvents [acetone, ethanol, n-hexane, and tetrahydrofuran (THF)] were of HPLC grade with ≥ 99% purity and purchased from RCI Labscan Ltd. Helium (> 99.999% purity) was used as the carrier gas. All labware used was glass or stainless steel to minimize background plasticizer contamination.

Reference plasticized PVC samples

Four types of reference samples Type-A: blank PVC; Type-B: PVC with a single type of plasticizer (BBP, DAP, DBP, DCHP, DEHP, DEP, DHP, DIBP, DIDP, DINP, DMP, DOA, DNOP, DEHT, DPP, MCCPs, and TOTM); Type-C: PVC with various combinations of two plasticizers [DEHP and MCCPs (with 1%, 5%, 25%, and 29% DEHP), DEHP and DINP (with 5%, 25%, and 29% DEHP), DINP and MCCPs (with 1%, 5%, 10% 15%, 20%, and 25% DINP), and DINP and DEHT (with 15% DINP)]; and Type-D: PVC with three plasticizers (DEHP, DINP and DEHT, 10% each) were produced in-house. Each sample was prepared by dissolving plasticizer(s) and PVC in THF at a temperature just below 60 °C, casting the solution on a petri dish, and allowing it to dry overnight in a fume hood to form a film. Each film was wrapped in aluminum foil and individually stored in zip-lock bags to prevent cross-contamination. All reference samples produced in-house were stored in a 25 °C air-conditioned room to minimize the sweating of plasticizers[2]. These samples were subsequently used as known plasticized PVC samples for Py/TD-GC-MS method development. The total plasticizer concentration of all in-house reference samples was kept at 30%. This high plasticizer concentration was intended to imitate the anticipated high concentrations in household samples investigated in this study. In particular, Type-C and Type-D samples were used to study and verify potential interactions and overlaps of MS responses from key target substances, namely DEHP, DINP, MCCPs, and DEHT.

Sample collection and pretreatment

Soft PVC samples were EOL products donated by coworkers and two local scrap shops in the Bangkok Metropolitan Area from December 2020 to March 2021. Only products made of flexible PVC were used, as identified by their high chlorine contents measured using a handheld energy-dispersive X-ray fluorescent spectrometer (Bruker S1 TITAN 800, USA). A total of 153 flexible PVC items, as shown in Figure 1, comprising 35 PVC boots, 56 wire and cable sheaths, 24 vinyl flooring sheets, and 38 garden hoses, were used in this study. As in local recycling practice, the PVC boots were separated into soles and ankle support parts for testing owing to their different flexibilities (i.e., plasticizer contents). Therefore, the total number of tested samples in the vinyl boot category was 43, and the total number of tested samples was 161. All samples were cleaned with mild detergent and deionized water, and air-dried. After cleaning, samples were individually kept in dark containers and stored in an air-conditioned room at 25 °C.

Chemical analysis

GC-MS (QP2010, Shimadzu Corp., Kyoto, Japan) with a pyrolyzer/thermal desorption accessory (Py-2020ID, Frontier Lab, Koriyama, Japan) was used in this study. Samples of approximately 0.5 ± 0.3 mg were each placed in a sample holder assembly for subsequent introduction into the pyrolyzer. All sample preparation tools used were metallic to prevent contamination, and were wiped clean with ethanol before and after each use. Furthermore, to avoid the carry-over of pyrolysis residue, the pyrolyzer sample holder assembly (stick and sample cup) was cleansed with a blowtorch before each use.

The Py/TD-GC-MS conditions (as shown in Supplementary Table 1) were based on standard IEC 62321-8, but adapted to accommodate a larger number of plasticizers (particularly non-phthalates and CPs) and target higher concentrations. Particularly, the pyrolyzer heating conditions were checked to confirm that no major decomposition of PVC and LMW analytes occurred while maintaining an acceptable desorption rate of HMW plasticizers (such as TOTM). Type-B reference samples with single plasticizers were used to obtain retention times and mass fragments of the target substances [Supplementary Table 2]. As this study aimed to simultaneously screen the target plasticizers in soft PVC samples, not to precisely quantitate each individual substance, the overall sensitivity of the GC-MS was decreased by increasing the split ratio and reducing the detector voltage, to reduce detector saturation incidents caused by samples containing high concentration(s) of highly responsive analyte(s). Samples were divided into weekly sets of about 70 samples.

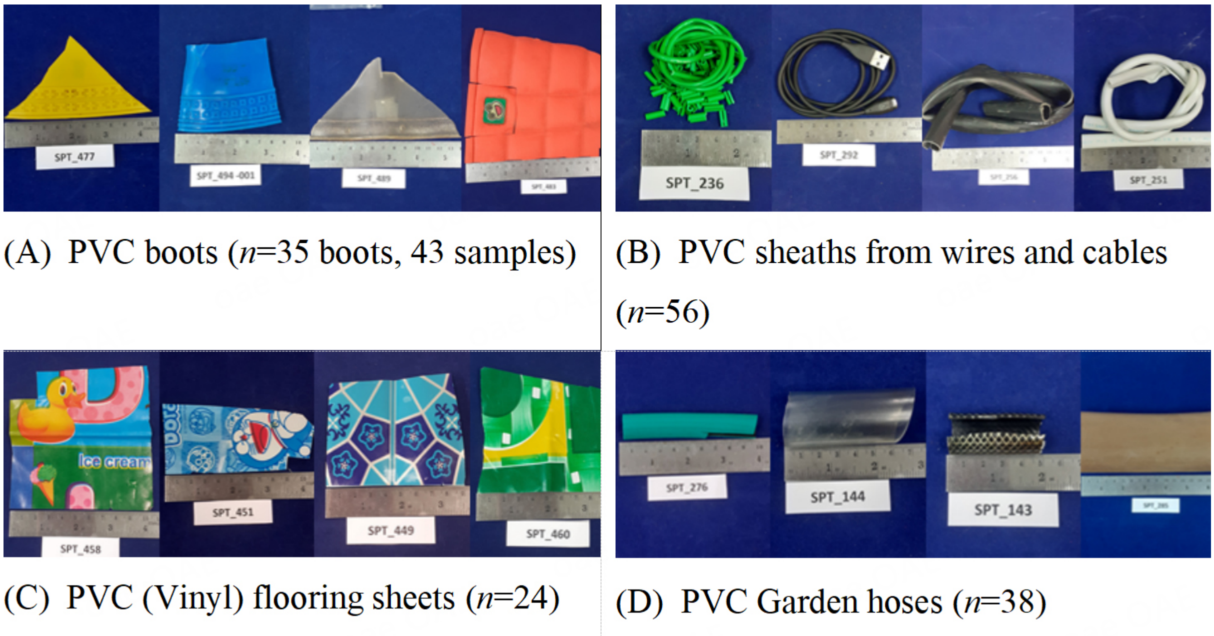

Figure 1. Flexible PVC samples analyzed in this study

The run order within each set was randomized to average out unknown factors. Furthermore, following each encounter of high-content sample (including detector saturation incidents), a Type-A blank sample or Type-B reference sample containing other plasticizer(s) was used to check for any carry-over of the high-content plasticizer. Furthermore, Type-B reference samples were tested after every nine samples to confirm proper system functionality.

MS data acquisition was performed in both full-scan (m/z range of 50-1000) and Selected Ion Monitoring (SIM) modes. Three GC-MS characteristics, namely the retention time and at least two characteristic ions (m/z), as shown in Supplementary Table 2, were used to confirm positive identification of each target substance. A characteristic retention time shift of about 0.1 min was allowed to accommodate possible peak broadening and interference among multiple coexisting plasticizers. As an exception, DINCH was the only plasticizer not included in the in-house reference sample group, but was instead identified using the built-in mass spectrum library and database, and a confirmation analysis of a product known to contain the substance.

Type-C reference samples were used to study the limits of identification and possible interactions among anticipated key plasticizers, namely, DEHP, DINP, MCCPs, and DEHT. Furthermore, reference samples with the most challenging combination (DINP and MCCPs mixture) were selected for linearity and repeatability studies.

Method verification with solvent extraction GC-MS

About 20% of samples from each of the four product groups were subjected to verification by the more precise ultrasonic solvent extraction and GC-MS (EI) method, as described in standard prEN IEC 62321-12:2022[64]. This standard method was modified to accommodate the identification of a larger number of targeted plasticizers (CPs, non-PAEs, and other non-validated PAEs) in soft PVC samples.

In particular, the oven temperature program was modified to reduce retention overlap between DHP and DEHP, DnOP and DEHT, and DINP and DIDP. The overall sensitivity of the equipment was reduced by decreasing the detector voltage to avoid detector saturation caused by the high concentrations of highly responsive target analytes, such as DEHP. Mixed plasticizer solutions and standard reference solutions (SCCPs, MCCPs, and mixed PAEs) were used to determine the characteristic retention times of the target plasticizers, and their observed characteristic fragment ion m/z values were verified against published sources[65-68]. Characteristic ions for DINCH, SCCPs, and MCCPs were adopted from the built-in MS library and database. To confirm equipment performance and check for signs of analyte carry-over between test runs, extraction blanks or control samples (reference solutions and standard reference solutions) were inserted into randomized test sequences every three runs.

The GC-MS measurement conditions established in this study are shown in Supplementary Table 3, and the GC-MS characteristic retention times and identification ions (m/z) are shown in Supplementary Table 4. Examples of the resulting (overlaid) GC-MS chromatograms obtained from five reference solutions (a 13-plasticizer mixed reference solution, two SCCPs standard solutions, and two MCCPs standard solutions) at m/z 79, 127, 141, 149, 293, and 307 are shown in Supplementary Figure 2.

RESULTS AND DISCUSSION

Performance of Py/TD-GC-MS method

The Py/TD-GC-MS total ion current (TIC) chromatograms (SIM mode) from Type-B reference samples, shown overlaid without normalization in Figure 2, clearly indicate that this method can be used to identify the targeted plasticizers. Furthermore, the chromatograms from Type-C samples containing mixed MCCPs and DEHP or DINP [Figure 3], and those from repeated tests of samples containing a mixture of 1% MCCPs and 29% DINP [Supplementary Figure 3], show possible retention time overlap, but can still be differentiated based on their respective identifying ions. As DINP and MCCPs, which are the least sensitive substances in our Py/TD GC-MS method, can be repeatedly identified at 1%, the limit of identification for all 18 target plasticizers (PAEs, MCCPs, and other non-PAEs) in this study is set to 1%. Notably, DINP and DIDP are mixtures of branched isomers, resulting in their chromatograms appearing as clusters of multiple low-intensity peaks. However, their GC-MS characteristics (retention times and at least two identifying ion masses) are distinguishable from the other plasticizers in this study, allowing their effective identification (see Table 2 for method performance).

Identification of plasticizers in soft PVC samples

A total of 153 soft PVC samples from EOL-PVC products, comprising 35 PVC boots, 56 wire and cable sheaths, 24 vinyl flooring sheets, and 38 garden hoses, were subjected to simultaneous plasticizer identification using Py/TD-GC-MS. Although all samples tested positive for at least one targeted plasticizer type, most samples contained three or more. This pattern was verified by the more precise solvent extraction GC-MS method (see next section).

Figure 4 shows example selected chromatograms of a typical cable sheath sample analyzed by Py/TD-GC-MS (m/z 79 and 125) and solvent extraction GC-MS (m/z 79, 127, 149, and 193). These Py/TD-GC-MS chromatograms clearly showed the presence of multiple plasticizers (DIBP, DBP, DEHP, DEHT, DINP, and CPs) in this sample, while the solvent extraction GC-MS result concurred with this finding. Although rigorous differentiation between SCCPs and MCCPs was not attempted owing to the lack of commercial SCCP reference samples for Py/TD-GC-MS, the very broad retention time range of the characteristic wavy chromatogram indicates possible mixing of both SCCPs and MCCPs in this sample. Precise differentiation of SCCPs and MCCPs using low resolution GC-MS would require the use of a chemical ionization mass

Table 2. Performance of the Py/TD-GC-MS screening method, as validated by ultrasonic solvent extraction GC-MS method

Indicator	BBP	CPs	DBP	DEHP	DEHT	DIBP	DIDP	DINCH	DINP	DOA	TOTM	Overall
True positive (TP)	1	23	7	27	11	2	0	0	19	6	6	102
True negative (TN)	32	10	22	4	19	31	33	32	9	20	13	225
False negative (FN)	0	0	4	2	3	0	0	1	5	7	14	36
False positive (FP)	0	0	0	0	0	0	0	0	0	0	0	0
Accuracy (%)	100	100	87.8	93.9	90.9	100	100	96.9	84.8	78.7	57.5	90.0
Precision (%)	100	100	100	100	100	100	NA	NA	100	100	100	100
Sensitivity (%)	100	100	63.6	93.1	78.5	100	NA	0	79.1	46.1	30	73.9
Specificity (%)	100	100	100	100	100	100	100	100	100	100	100	100
F1-Score (%)	100	100	77.7	96.4	87.9	100	NA	NA	88.3	63.1	46.1	84.9

NA: Not available (due to zero incident).

selective detector (NCI), as described in ISO 18219-1 and 18219-2: 2021 and ISO 22818: 2021[69-71] standards, which is beyond the scope of this study.

An itemized list of targeted plasticizers detected in every sample is provided in Supplementary Table 5. DEHP, CPs, and DINP are the three most common plasticizers, with frequencies of detection (FOD) of 81%, 65%, and 61%, respectively. The patterns of plasticizers found appear to differ across different product groups, as shown in Figure 5 (FOD of each plasticizer) and Figure 6 (number of plasticizers within each sample).

Vinyl boots

DEHP is the main plasticizer found in this product group (93% FOD), followed by DINP (65.1% FOD). Compared with the other three product groups, CPs are least often detected in vinyl boots (30.2% FOD). Other non-PAEs (DEHT, TOTM, and DOA) are also found at moderate frequencies (20%-30%). DINP is not detected alone (singular), but in combination with other plasticizers, especially DEHP. Similarly, singular DEHP and binary DEHP-CPs combinations are found in only 16.3% and 4.7% of the samples, respectively, while any plasticizer combination with both DEHP and DINP make up 60.5% of the total samples. About 30% of the samples have CPs as the secondary plasticizer, with either DEHP or DINP as primary plasticizer, about half of which contain both DEHP and DINP. Interestingly, more than half of the samples (51.2%) in this PAE-dominat sample group also contain non-PAEs at lower levels (but high enough to be detected). Only one sample was found to contain singular non-PAE (DEHT).

Vinyl boots are highly plasticized. Most samples (58.1%) contain three or more plasticizers, with one sample containing as many as seven plasticizers [Figure 6]. Notably, the restricted DEHP and as-yet-unrestricted DINP are frequently found together (60.5%). Among these, 23% were binary DEHP-DINP mixtures, while the majority (77%) were in combination with other plasticizers, namely, DEHT (50%), TOTM (40%), CPs (35%), DOA (30%), and DBP (20%).

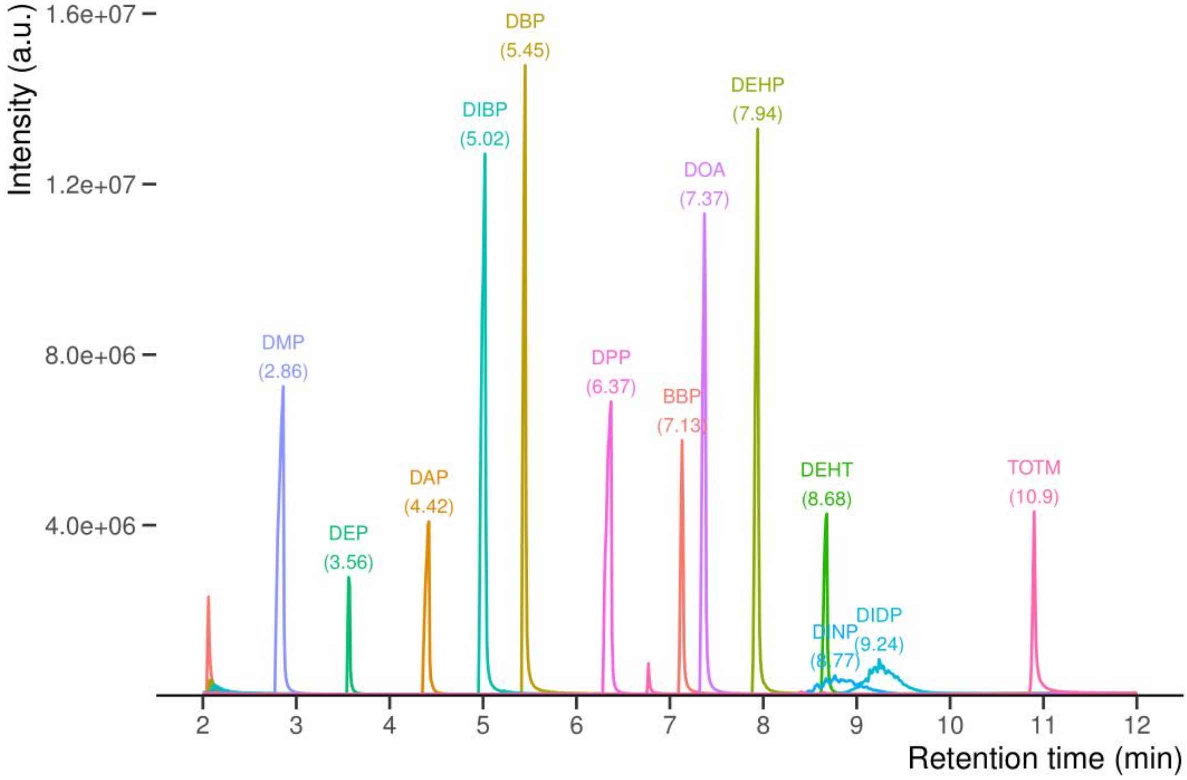

Figure 2. Py/TD-GC-MS total ion current chromatograms (SIM mode, overlaid, without normalization) from reference plasticized PVC samples, each with 30% of designated plasticizer and 70% virgin PVC resin.

Cable sheaths

For the other three product groups, DEHP appears to be the primary plasticizer used, with CPs as the secondary plasticizer. However, in cable sheaths, DEHP has been replaced by DINP (76.8% FOD), while the FOD of CPs as secondary plasticizer remains high (78.6%). DEHT and TOTM are also detected, but at lower frequencies (15%-20%), and mostly mixed with DEHP. However, compared with other product groups, the detection rates of DEHT and TOTM in wire and cable sheaths are relatively high. DIDP is also found, albeit at a very low FOD (5.4%). Although Thailand has yet to enforce domestic controls similar to the EU RoHS Directive, this shift in pattern indicate the influence of EU Regulations on the contents of hazardous substances in Thai electrical and electronic equipment (EEE).

As shown in Figure 6, cable sheaths mostly comprise two or more plasticizers (91%). Only five samples contain singular plasticizers, four with DEHT and one with DEHP. The most frequent combinations are binary DINP-CPs mixtures (35.7%), followed by ternary DINP-DEHP-CPs blends (17.9%). The mixing of restricted and non-restricted plasticizers is also found in this application group, but to a lesser extent. Among the 43 samples containing DINP (76.8% of all sheath samples), 46.5% also contain CPs and non-restricted PAEs, and 53.5% are blended with CPs and restricted PAEs. This pattern further implies the influence of global regulations on EEE marketed in Thailand.

Vinyl flooring sheets and mats

All vinyl flooring samples tested contain DEHP. Most also contain CPs (62.5% FOD) and DINP (70.8% FOD). BBP, the only polar plasticizer in this study, is only found in this application group. Interestingly,

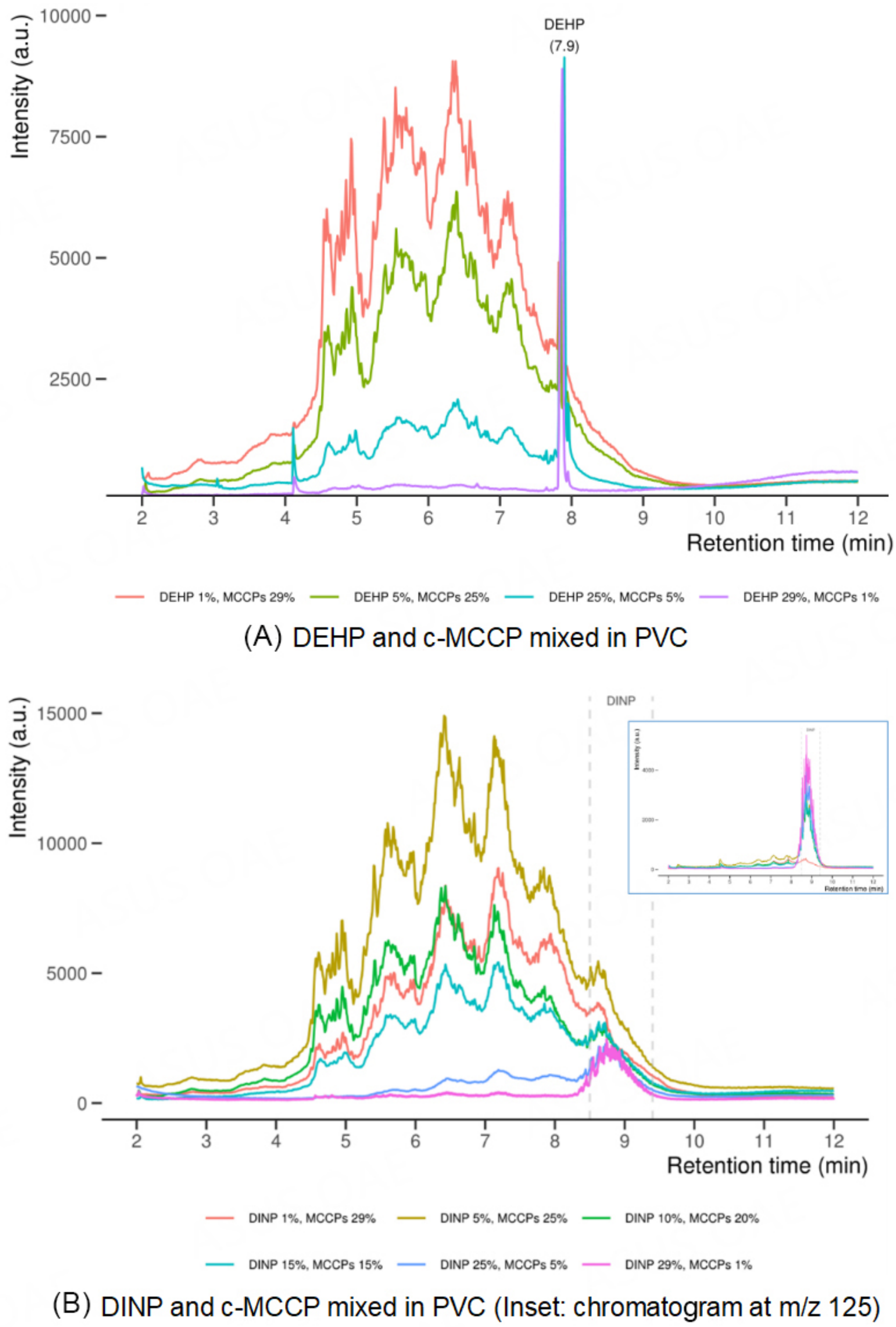

Figure 3. Py/TD-GC-MS chromatograms (SIM mode, m/z 79) from Type-C reference PVC samples with (A) DEHP and c-MCCP mixtures, and (B) DINP and c-MCCP mixtures. The very broad and wavy undulating response of c-MCCP is clearly differentiated from the sharp single spike of DEHP, and the narrower cluster of multiple isomeric congener peaks of DINP.

samples with BBP do not contain CPs, but rather blended with DEHP or DINP. Compared with the other three product groups, the number of plasticizer types found in this group is lower (six substances). However, about 67% of the samples tested contain more than two plasticizers, of which 62.5% contain the main trio of DEHP, DINP, and CPs, with and without a fourth plasticizer (usually DEHT).

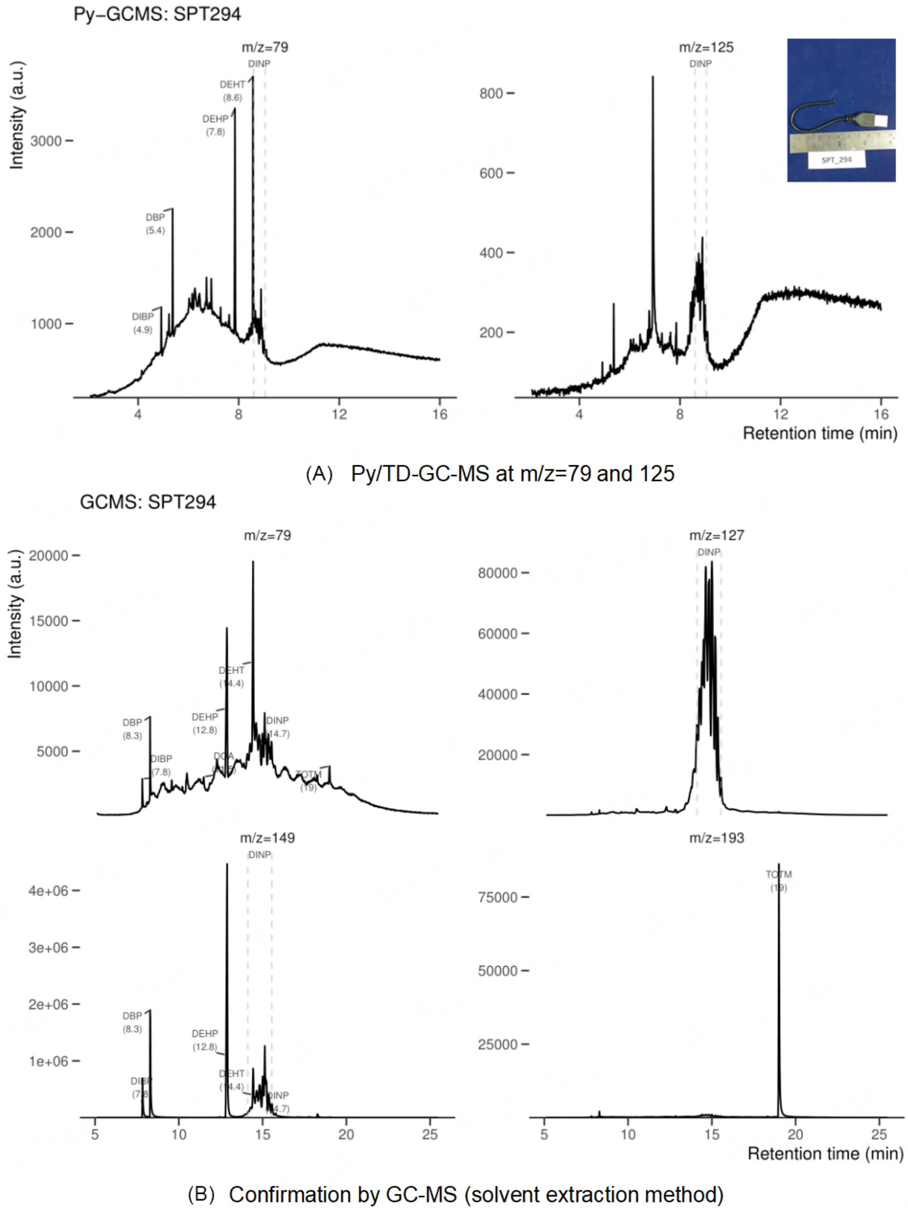

Figure 4. Demonstration of (A) Py/TD-GC-MS chromatograms (SIM mode, m/z 79 and 125) from a sample (cable); and (B) the corresponding GC-MS chromatograms (SIM Mode, m/z 79, 127, 149 and 193) from solvent extraction method.

Garden hoses

The plasticizers found in garden hoses are predominantly binary DEHP-CPs blends (66.7% FOD). The FOD of DEHP is also very high (94.7%), with only 2 of 38 total samples not containing DEHP. Compared with the other product groups, the FOD of non-restricted PAEs and non-PAEs are very low, and all samples also contain restricted PAE(s). About 16% of the samples contain DINP, all of which are mixed with DEHP, while half are also mixed with CPs and, surprisingly, DIDP and TOTM.

Patterns of plasticizers used in garden hoses are less complex compared with those in the other product groups. Most are binary systems (79.5%), among which most are DEHP-CPs blends (83.9%). Although limited, samples with more than two plasticizers also contain DEHP and CPs. This might be because most

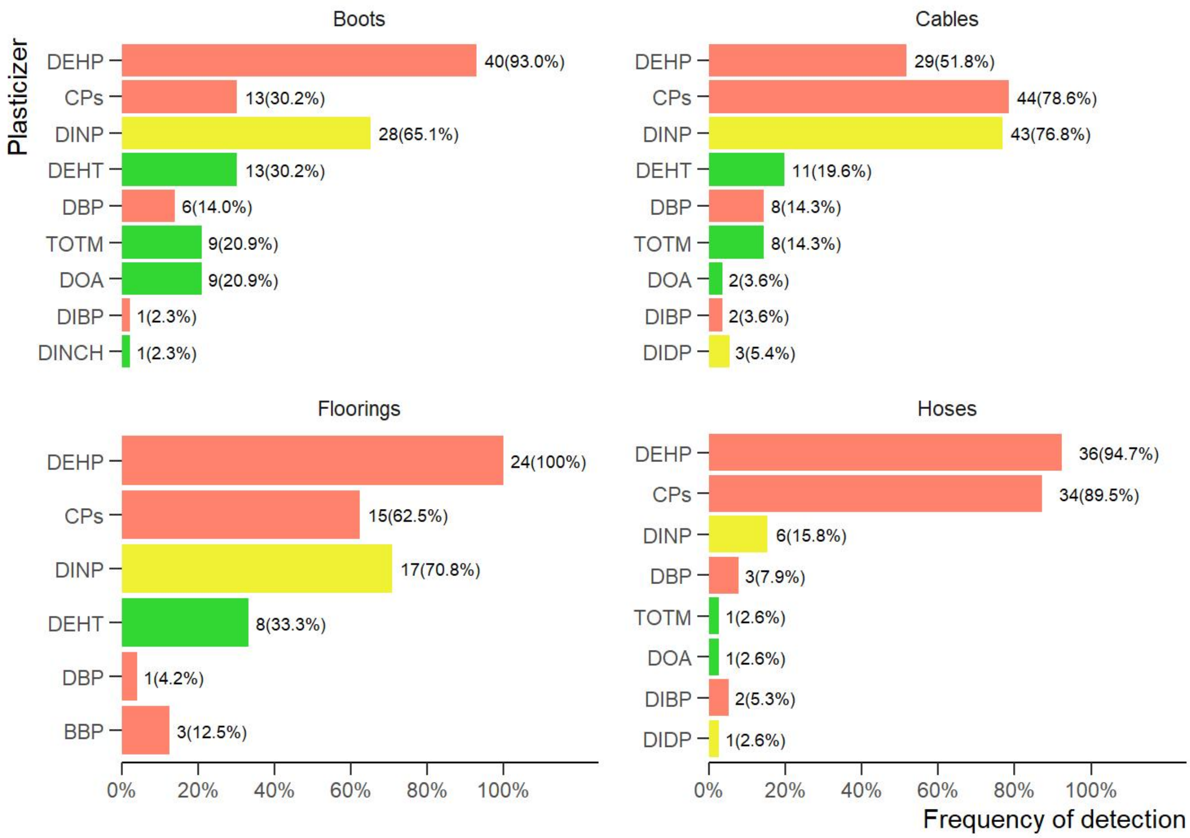

Figure 5. Frequency of each plasticizer detected by Py/TD-GC-MS. The mixture of DEHP and CPs is the most common popular plasticizer combination, except for cable sheaths where DEHP has been replaced by DINP. Red bars: restricted plasticizers; Yellow bars: yet to be widely restricted PAEs; Green bars: non-PAEs alternatives.

samples in this study are clear hoses, which are less likely to contain post-consumer recycled feedstocks. Only one clear hose sample contain the binary DEHP-DINP mixture. All hose samples found to contain DINP and DIDP are colored and opaque.

Verification of Py/TD-GC-MS identification results

About 20% of samples were also subjected to the more precise solvent extraction GC-MS method, as described in section 2.5. The identification results from both methods are compared using a confusion matrix that considers four parameters, namely, true positive (TP), true negative (TN), false positive (FP, also known as Type-I error), and false negative (FN, also known as Type-II error). TP represents the number of samples for which both Py/TD-GC-MS and extraction GC-MS yield positive identification for a particular plasticizer. Similarly, TN represents the number of samples for which both methods yield negative identification for a particular plasticizer. In contrast, FP represents the number of samples that Py/TD-GC-MS identifies as positive for a particular plasticizer, while extraction GC-MS 122 does not. Finally, FN represents the number of samples that extraction GC-MS identifies as positive for a particular plasticizer, while Py/TD-GC-MS does not. The four confusion matrix values for all identified plasticizers are shown in Table 2.

The performance of Py/TD-GC-MS is further analyzed using five figures of merit, namely, accuracy, precision, sensitivity, specificity, and F1 score, as defined in Supplementary Table 6. The calculated

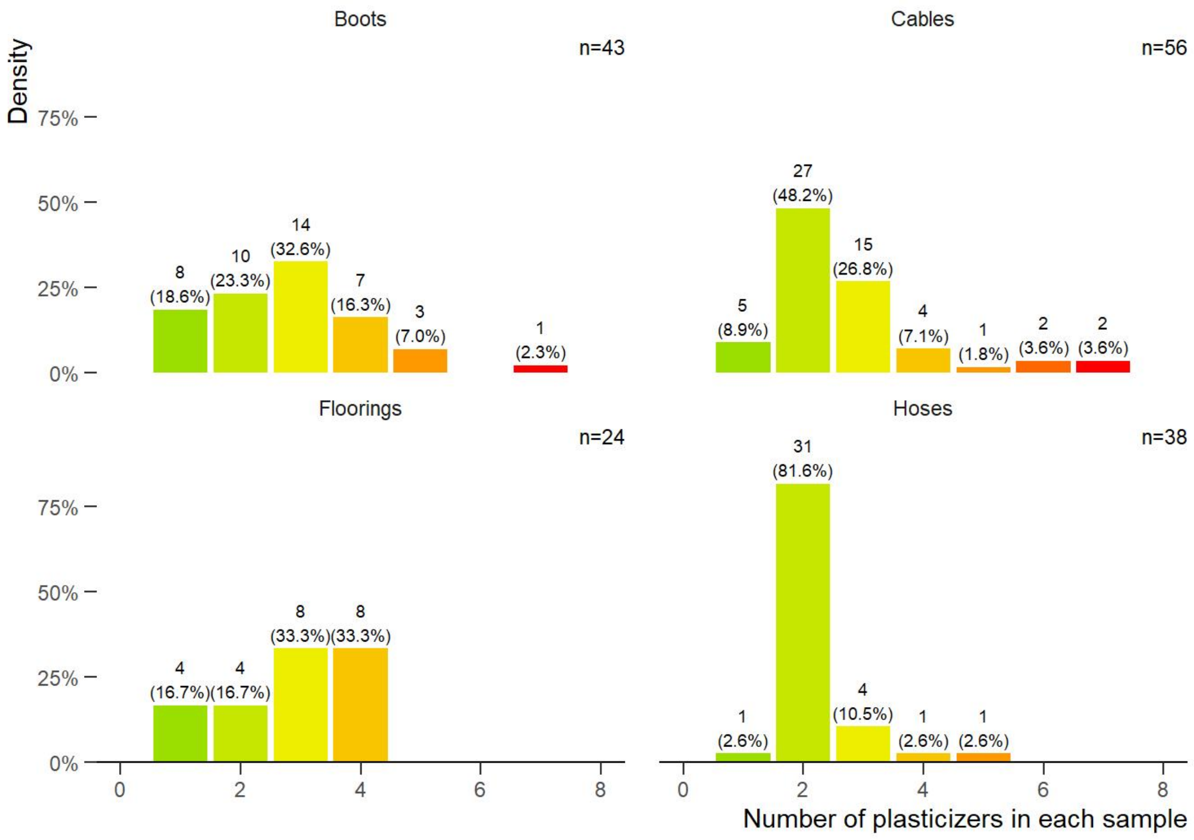

Figure 6. High number of plasticizers within each sample indicating a high degree of feedstock mixing from diverse sources.

performance of Py/TD-GC-MS for the identification of plasticizers in this study is shown in Table 2.

The Py/TD-GC-MS method employed in this study aims to simultaneously screen plasticizers contained in soft PVC items. The performance evaluation results clearly indicate that the method offers high precision for all positively identified plasticizers. The method is also very specific, producing no false positives. All Py/TD-GC-MS positive identifications are confirmed by GC-MS. However, owing to its inability to identify certain substances at low concentrations, particularly TOTM and DOA (high FNs), this method exhibits low sensitivity and, consequently, provides low accuracy for the identification of these plasticizers in samples. Other substances that also suffer some FNs are DINP, DBP, DEHT, DEHP, and DINCH. These FNs led to reduced sensitivity, which was the trade-off for the versatility of this Py/TD-GC-MS method. However, the detection accuracy for these five plasticizers was still approximately 85% or higher, and the overall accuracy of 90% is rather satisfactory.

Discussion

This study has shown that Py/TD-GC-MS can be used as a complementary screening technique for simultaneous identification of multiple plasticizers, as confirmed by the more precise solvent extraction GC-MS method. The Py/TD-GC-MS method saves time and resources while providing sufficiently high accuracy for most of the relevant plasticizers. This method is also robust against cross-contamination and common ambient levels of DEHP and DBP. Although the overall sensitivity of detection is somewhat low due to the adjustment made to accommodate the disproportionately high DEHP response, future adjustment can be made to render the method more sensitive to selected plasticizer species, as needed.

Although 18 plasticizers were targeted, only 11 were detected in our samples. The absence of the other seven plasticizers (DAP, DCHP, DEP, DHP, DMP, DnOP, and DPP) is consistent with Thailand's plasticizer production and consumption profiles. Apart from BBP, which was found in some PVC flooring samples, the other LMW PAEs (DMP, DEP, DAP, and DPP) are likely not generally used in these four product groups, but are instead used as solvents in applications such as perfumes, inks, and other personal care products[72-74].

Although PAEs and CPs are generally known to be incorporated together as primary and secondary plasticizers in the same PVC products, the number of studies on their usage patterns in household products is limited. Our results reveal the cocktail-like plasticizer patterns, to varying degrees, in all four groups of soft PVC products. If 'cocktail-like' patterns are defined as combinations with four or more plasticizers, then close to 20% of the soft PVC samples tested contain 'plasticizer cocktails', which is a rather alarming portion. The current Py/TD-GC-MS method is not sensitive to most plasticizers at low concentrations (below approximately 1%), implying that such 'cocktails' could not have resulted from incidental contamination. Furthermore, unlike the inadvertent contamination observed in other recycled materials (such as plastic waste[51] and food-contact packaging[75-77]), the level of plasticizers found in our samples are above the decimal fraction percentage range. These observations, in combination with relatively and sustainably high EOL PVC buy-back prices offered by scrap shops, suggest that 'indirect' recycling of plasticizers via mechanical recycling of PVC has been a common practice, at least for products available on the Thai market. Similar 'indirect' additive recovery via mechanical recycling is practiced in industry, such as flame retardant recovery[78], with some having caused exposure concerns[79-82].

In general flexible PVC production practice, there is no obvious incentive to apply several types of plasticizers to any individual product, especially if they serve the same function[83]. In business terms, using diverse but redundant ingredients only increases the operation cost and burden, even more so if the substances are restricted. Increasing international restrictions on several groups of plasticizers should, instead, discourage producers from marketing soft PVC products that contain both restricted and non-restricted plasticizers. Based on our results, binary combinations of only two plasticizers, one primary and one secondary, are available on the market (as exemplified by a large proportion of our hose and cable sheath samples). However, some samples contain up to seven different plasticizers, which can most likely be attributed to uncontrolled mixing caused by open-loop recycling activities, where inputs (possibly from multiple sources) are selected mainly for their price and functionality. Such uncontrolled mixing of potentially hazardous plasticizers into common, low-priced products could expose consumers (particularly the underprivileged, toddlers, and young children) to harmful plasticizers. Without proper controls, such naïve practice will only be aggravated in the CE era, for both PVC and other recyclable plastics in general[75,76].

Certain human health outcomes have been attributed to exposure to PAEs, including lowered semen quality, neurodevelopmental disorders (such as attention deficit hyperactivity disorder), childhood asthma, and effects on anogenital distance in boys[84]. Effects of CPs on human health include hepatic enzyme induction and thyroid hyperactivity[85]. Specifically, SCCPs are classified as suspected to cause cancer (Category 2B) by the International Agency for Research on Cancer[86] and listed as endocrine disruptors by the EU[85]. SCCPs are also known to be persistent, bioaccumulative in humans and wildlife, and toxic to aquatic organisms at low concentrations[85].

In terms of human monitoring efforts, existing studies report either metabolites of PAEs and non-PAE alternatives in urine[87-90], or CPs in blood[91-94] and breast milk[95,96]. Unfortunately, to our knowledge, both groups of plasticizers have yet to be monitored together within the same set of subjects. Regarding primary plasticizers, a key common finding from existing studies is that multiple PAEs and PAE alternatives (as many as 17 substances[97]) are present together in individual human subjects, which is attributed to exposure to multiple sources. Some human monitoring studies also attempt to correlate these plasticizers of concern with their sources using questionnaire surveys[89,90]. Investigations into the sources of primary plasticizers have mainly focused on 'usual suspect' sources that are already regulated, including food-contact materials, toys and childcare items, personal care products, and medical devices[18-27]. Reports on additional indoor sources of primary plasticizers are emerging[98-100], such as the work by Promtes *et al.*, who attributed elevated levels of DEHP and DINP in dust collected from Thai homes to PVC flooring materials and other 'usual suspect' objects[101]. The prevalence of these two PAEs were mirrored by our results, as well as other reports[24].

Regarding CPs as secondary plasticizers, the "Fourth Coordinated Survey of Human Milk for POPs" recently published by WHO[96] revealed alarmingly high CP levels already approaching those of the infamous insecticide DDT, and are likely to surpass all other POP substances in the near future, warranting urgent intervention. Existing studies indicate that human exposure occurs through ingestion of contaminated food[93,102,103] and dust[104-107]. The main sources of CPs in developing countries appear to differ from those in developed nations[96]. Although McGrath *et al.* (2021)[28] and Guida *et al.* (2022)[29] reported relatively low levels of CPs (< 1%) in the Belgian and Japanese markets, respectively, studies by Wang *et al.* (2018)[30] and Chen *et al.* (2021)[31] reported high CP detection frequencies in cable sheaths, PVC floorings, and PVC hoses collected in China, with concentrations often exceeding 10%. Again, the prevalence of CPs identified by these studies mirrors our current results. The present work is among few existing studies[60] report the copresence of CPs and primary plasticizers of concern in household products. Along with DEHP and DINP, CPs were prominent in most of our samples, both in terms of detection frequency and concentration level. However, owing to the difficulty of CP analysis[108], the number of studies on CPs in products remains limited. Adequate, representative, and timely analysis that would help pinpoint the actual sources of these substances for different economic regions is urgently required. The need to identify products that contain CPs and other plasticizers of concern is especially relevant in the context of the current global drive towards CE.

CE actions can improve resource utilization efficiency. However, the transition toward CE is blamed by many for helping prolong and spread toxic substances[24]. For converters in Asia, cost reduction is currently the main incentive for incorporating recycled plasticizers, and a reverse value chain for soft PVC items appears to be well established. Furthermore, buy-back prices for EOL soft PVC products are attractive. As a result, EOL PVC products that arrive at scrap shops are well segregated, not only by product groups, but also by color. Converters of 'new' PVC products that use recycled PVC as a feedstock probably have some knowledge of the functionality of embedded plasticizers, but not their specific identities or associated risks and restrictions. Although in terms of CE, indirect plasticizer recycling appears to help such entrepreneurs save money and resources[109], unaffected materials feedstocks will also turn into contaminated materials, drastically lowering their circular value.

Unregulated recycling of affected plastic items will lead to an exponential growth in the number of affected products. Without sufficient controls, the spread of hazardous additives via recycling activities represents a significant public health challenge, particularly among developing nations[79,84,110], as well as the significant financial burden eventually required to organize proper management of the affected materials. To prevent the spread and intermixing of hazardous plasticizers, materials users and responsible authorities need to be aware of the identity, presence, and risk associated with all relevant plasticizers in products, starting with the communication of chemicals in products (CiP) from their first lifecycle and beyond. Users of materials in each of the subsequent cycles must be informed of the constituent CiPs. Therefore, CiP communication should be a required duty for every actor incorporating substances into products, such as that described in the material passport systems[111,112].

Furthermore, recyclers and their downstream converters can also assure the safety of materials/products if their starting feedstocks are traceable, and if screening tests are accessible and affordable. Finally, policies and measures to remove affected materials from circulation must be planned and executed, and the contaminated materials must be directed to proper pathways, which can be assisted by research and innovation.

CONCLUSION

Our study has demonstrated a successful application of Py/TD-GC-MS to simultaneous screen PAEs, PAE alternatives, and CPs in four groups of soft PVC products. The method is fast and economical, allowing analysis of a sufficiently large number of samples to reveal plasticizer usage patterns. For the first time, this study shows the widespread intermixing of several plasticizers, both restricted and non-restricted, in selected product groups that can come into close and prolonged contact with users, especially children. As there is no obvious incentive for producers to intentionally apply many types of plasticizers to each individual product, this intermixing can be attributed to uncontrolled open-loop recycling. The risk associated with such indirect recycling of plasticizers via mechanical recycling of soft PVC can be mitigated by transparent communication of chemicals in products, among other measures.

DECLARATIONS

Authors' contributions

Conceptualization, methodology, validation, supervision: Ramungul N
Investigation: Viwatthanasittiphong P, Chuayrueng N, Koonhorm S, Ausavanonkulporn A
Formal analysis, visualization: Ramungul N, Temtanapat Y
Writing original draft, project administration: Ramungul N, Boontongkong Y
All authors read and approved the final manuscript.

Availability of data and materials

Data supporting the findings can be found in supplementary materials.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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