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RESEARCH ARTICLE

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# A comparative assessment of the use of suitable analytical techniques to evaluate plasticizer compatibility

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**Abstract**

The evaluation of novel phthalate-free plasticisers for PVC formulations is hindered by the lack of a reliable quantitative method for testing plasticizer exudation from PVC formulations. Two methods of improving upon the ASTM D3291 exudation test have been trialed using ATR-FTIR and GC–MS. The results of these methods are compared alongside a study of the glass transition temperatures ($T_g$) by dynamic mechanical analysis (DMA). FTIR is found to be unsuitable for determining plasticizer exudation as the method is not sufficiently sensitive to detect small changes in plasticizer distribution. Carbonyl peak positions in unstressed samples are instead investigated to determine the strength of interaction between the plasticisers and PVC chain. GC–MS is successfully used to quantify plasticizer exudation that could not be observed visually or by FTIR. Furthermore, these methods show limited correlation to each other, which highlights the importance of testing multiple aspects of compatibility when developing novel plasticisers for use in PVC.

**KEYWORDS**
compatibility, exudation, phthalates, plasticisers, polymers, polyvinyl chloride

## 1 | INTRODUCTION

PVC is one of the most commonly used polymers, with applications in areas such as construction, food packaging, electrical insulation, clothing and toys.[1] Plasticisers are added to the polymer to soften the material and modify the properties to allow for the wide range of applications in which it is used. The plasticisers most commonly used in PVC are external plasticisers – that is, the plasticizer is not chemically bonded to the polymer.[2] These plasticisers typically have low volatility and low to medium molecular weights. Historically, PVC plasticisation has been dominated by phthalate esters, which were one of the earliest plasticizer types used in PVC.[2] Dioctyl phthalate (DOP or DEHP, Figure 1-**1**) was the most widely used plasticizer in PVC formulations until recent years. As of 2015, it represented only 13% of the EU plasticizer market.[3] This is largely due to safety concerns – studies have suggested that DOP may have carcinogenic and endocrine-disrupting properties.[4,5] The addition of DOP and other phthalates to the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) SVHC (Substances of Very High Concern) list,[6] and other legislation such as the Safe Drinking Water and Toxic Enforcement Act of 1986 (also known as Proposition 65) in California, has limited the use of these plasticisers in
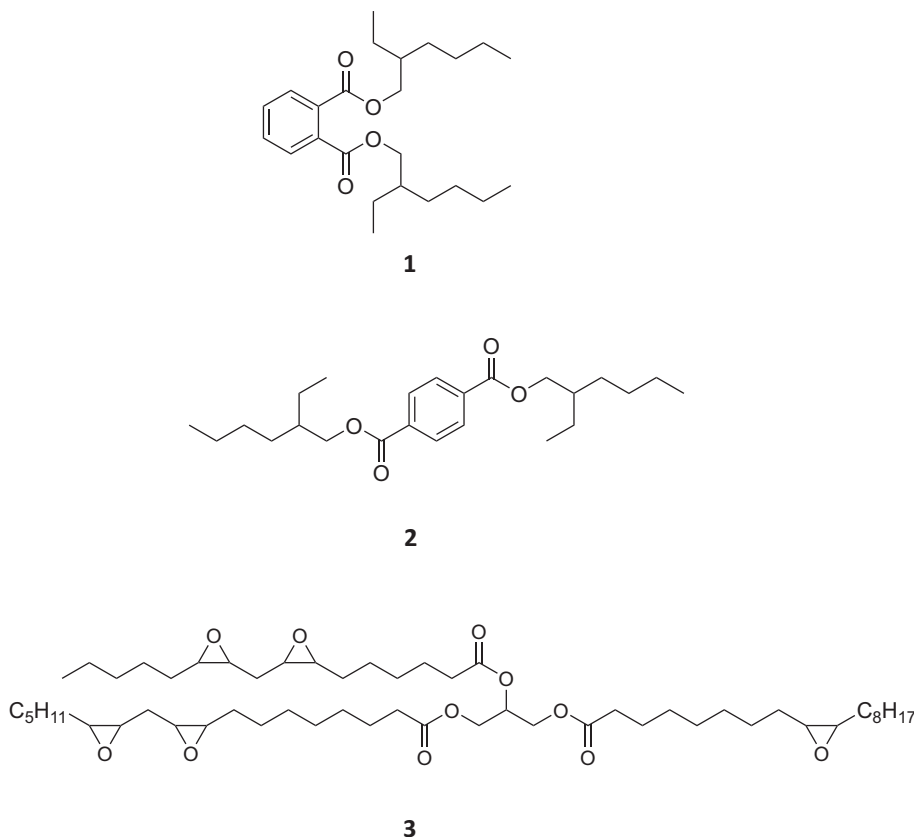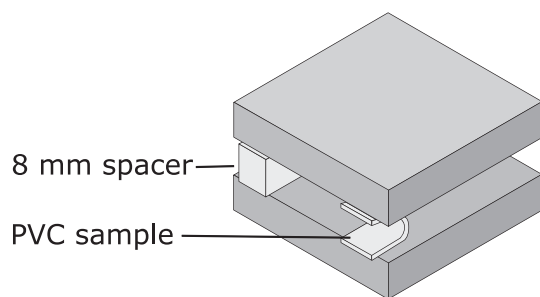
**1**



**2**



**3**

**FIGURE 1** Chemical structures of three plasticisers used in PVC formulations – diethylhexyl phthalate (DEHP or DOP, 1), diethylhexyl terephthalate (DOTP, 2) and a representative component of epoxidised soybean oil (ESBO, 3).



**FIGURE 2** Diagram of the ASTM D3291 loop spew test for plasticizer compatibility in PVC.[10]
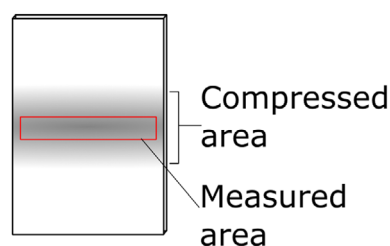


**FIGURE 3** Diagram of compressed PVC sample showing the stressed portion and the target area for FTIR measurement. [Color figure can be viewed at wileyonlinelibrary.com]

PVC compounding.[2] This has created a gap in the market, leading to the development of many alternative plasticisers, such as terephthalates, citrates, adipates and sebacates.[1,2] One widely used terephthalate is the para isomer of DOP, dioctyl terephthalate (DOTP, Figure 1-2).[1,7] Although the two plasticisers are similar in structure, it has been shown that DOTP does not pose the same health risks as DOP due to the difference in metabolites formed by the two compounds in the body.[1,5]

However, both phthalates and terephthalates are largely synthesized from petrochemicals. As environmental pressure increases, the demand for renewable, bio-based plasticisers has grown.[2] Plasticisers can comprise

more than 50% of the total weight of a flexible PVC formulation. As such, replacing petrochemical plasticisers with bio-based alternatives can significantly reduce the environmental footprint of the finished product, despite the typically petrochemical-based PVC polymer.

Plant-based oils derived from sunflower oil, castor oil, linseed oil and soybean oil have been used as PVC plasticisers, following an epoxidation reaction.[2] This increases the polarity of the fatty acid chains in the oils and gives rise to a stronger interaction with the PVC chain.[8] Epoxidised oil plasticisers such as ESBO (epoxidised soybean oil, Figure 1-3) are typically used as a secondary plasticizer in combination with a primary plasticizer, as compatibility is thought to be lower.[2] The epoxide functionality provides

an additional benefit to the PVC compound, as it acts as an acid scavenger and so improves the thermal stability of the material.[9]

Despite the many developments in alternative plasticisers for PVC, the methods for evaluating these plasticisers have not shown similar progress, particularly regarding plasticizer compatibility. ASTM D3291 "loop spew" test is one method for testing plasticizer compatibility in PVC compounds.[10] This method involves stressing a sample of PVC compound in a loop, as shown in Figure 2. Plasticizer exudation is then judged visually on a scale from 0 (no exudation) to 3 (heavy exudation). This method is based on a subjective judgment which may be unreliable. A more quantitative analytical method would allow PVC compounders to compare and record useful information about the compatibility of different plasticisers. The techniques typically available to laboratories in the PVC compounding industry must be considered – fourier transform infrared (FTIR) and gas chromatography - mass spectrometry (GC–MS) are commonplace, while techniques such as NMR (nuclear magnetic resonance) or UV–Vis spectroscopy are not.

Plasticizer exudation can lead to a number of undesirable properties in a PVC formulation. At low levels it can cause a tacky surface finish and poor clarity, while at higher levels it can lead to environmental contamination of air, water or food products as well as a degradation in the properties of the PVC article.[11,12] As such, minimizing plasticizer exudation is of high concern for PVC formulators.

FTIR (Fourier Transform Infrared) spectroscopy has been used in a number of works to examine the strength of the interaction between plasticisers and PVC.[13–17] The most common plasticizer types (phthalates, adipates etc.) all contain carbonyl functional groups. These polar groups are attracted by dipole forces to the polar carbon-chlorine bond in PVC and can also hydrogen bond to the α-hydrogen.[15] These attractive forces hold the polymer and plasticizer molecules together within the PVC compound. This interaction slightly weakens the carbon–oxygen double bond in the plasticizer, and the stronger the attractive force between the molecules, the more this bond is weakened. This weakening of the carbonyl bond can be observed by FTIR spectroscopy as a shifting of the C=O stretching band to a lower wavenumber. Some works have used the magnitude of this weakening as a definition of plasticizer compatibility.[16] However, the strength of the interaction between the plasticizer and PVC is not the only determining factor in plasticizer exudation. The size and shape of the plasticizer molecule, and therefore the ability of the plasticizer to move freely through the polymer matrix, will also affect exudation.

The vast majority of studies on plasticizer loss from PVC are concerned with evaporative loss at elevated temperatures, or loss to a liquid extractant medium.[18–21] Plasticizer loss resulting from mechanical stress (such as in the ASTM D3291 method) is less frequently studied, even though there are numerous applications for plasticised PVC where mechanical stress is far more likely to occur than solvent contact or raised temperatures, for example window gaskets. While the use of GC–MS for plasticizer analysis is well known, for example in measuring plasticizer extracted into solvents or food simulants,[6] it has not yet been explored as a way to add quantification to the loop-spew test for exudation. Investigations into plasticizer compatibility also tend towards studying single-plasticizer systems.

Plasticizer compatibility is also frequently measured by the suppression of the glass transition temperature of the polymer, usually measured by differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA).[22,23] Effective plasticisation lowers the glass transition temperature of a polymer to below the operating range of the product, allowing for flexible rubbery behavior. Incompatibility between the plasticizer and polymer can cause phase separation within the material, which can be observed by the presence of broad or multiple glass transition temperatures within a sample.[24]

Despite the many works to develop an understanding of PVC technology and evaluate plasticisers in PVC compounds, there is still no generally accepted method to quantitatively determine the amount of exudation by a plasticizer from a PVC matrix, especially not in so far as it concerns the newer, more sustainable plasticisers derived from biobased resources. Neither is there significant work correlating plasticizer exudation to other methods of testing plasticizer compatibility in PVC such as the suppression of glass transition temperature. This investigation therefore aims to find alternative, objective, and qualitative and quantitative instrumental analytical methods to determine the presence and level of exudation of plasticisers from PVC, as well as comparing it with the ASTM D3291 standard method.

## 2 | MATERIALS

All materials used to produce the PVC samples were provided by Alphagary Ltd. Chemicals used were ethanol (absolute, VWR), 1-Ethyl Naphthalene ($\geq$97%, Aldrich), sodium citrate (99%, Aldrich), dimethyl pimelate (99%, Aldrich), sodium ethoxide (21% in ethanol, Alfa Aesar), Methyl tert-butyl ether (MTBE, 99.8%, Sigma Aldrich), n-hexane (>97%, Honeywell), magnesium sulfate (Laboratory reagent grade, Fisher Scientific).

**TABLE 1** PVC formulations based on single and mixed plasticizer systems in PHR (per hundred resin) and percentage (%).

| Formulation | 1 PVC-DOTP | 2 PVC-DOP | 3 PVC-ESBO | 4 PVC-DOTPESBO | 5 PVC-DOPESBO |
|---|---|---|---|---|---|
| PVC K70 resin [PHR] [percentage] | 100 58.6% | 100 58.6% | 100 58.6% | 100 58.6% | 100 58.6% |
| Ca/Zn heat stabilizer | 0.6 0.4% | 0.6 0.4% | 0.6 0.4% | 0.6 0.4% | 0.6 0.4% |
| DOTP | 70 41.0% | - | - | 35 20.5% | - |
| DOP | - | 70 41.0% | - | - | 35 20.5% |
| ESBO | - | - | 70 41.0% | 35 20.5% | 35 20.5% |

# 3 | EXPERIMENTAL

## 3.1 | Sample preparation

Samples of plasticised PVC were prepared by cold mixing of plasticisers, PVC resin and heat stabilizer additives, followed by compounding with a Farrel two-roll mill at 155°C for 5 min. The formulations tested are shown in Table 1. Per hundred resin (PHR) is a commonly used convention for PVC compounding, where components are listed relative to 100 grams of PVC resin.

The samples were compression molded in a Mackey-Bowley heated hydraulic press at 170°C and 200 bar pressure for 4 min to produce plaques of 2 mm thickness. The 2 mm thickness pressed plaque was cut into samples with dimensions $25 \times 30$ mm.

## 3.2 | Compression loop test

Samples were prepared and stressed in the loop spew test as described in ASTM D3291 (Figure 2). The sample pieces were inserted between metal plates separated by spacers 8 mm thick. The test pieces were compressed over a range of time periods, then removed and tested for plasticizer exudation. Individual sample pieces were prepared for each measurement and discarded after testing. Exudation was measured using visual examination of a test paper as in the ASTM method, by FTIR spectroscopy and by GC–MS analysis.

## 3.3 | Fourier transform infrared spectroscopy (FT-IR)

FTIR spectra were measured on a Nicolet iS5 with iD5 ATR attachment. FTIR was used to measure the surfaces

of the samples stressed by the compatibility test in the area where plasticizer would exude, that is, the compressed face of the looped sample, Figure 3. The sample was removed from the compression plates, the centre of the stressed area was placed on the ATR crystal and clamped in place to ensure good contact with the crystal. Five samples of each formulation were measured for each time point. 16 scans were collected for each spectrum, the spectral resolution was set to 4 cm$^{-1}$ and the data spacing was 0.482 cm$^{-1}$. FTIR spectra were also collected for the individual plasticisers, as well as representative mixtures of the plasticisers (1:1 DOTP-ESBO and 1:1 DOP-ESBO), corresponding to the mixed plasticizer formulations.

## 3.4 | Gas chromatography—mass spectroscopy (GC–MS)

GC–MS analysis was used to quantify plasticizer exudation following the loop spew test. The inner surface of each sample, where the exudation occurs, was wiped with an analytical cotton swab in a set pattern covering the surface of the sample. The swabbing procedure ensured that every part of the compressed area was swabbed twice in each of two perpendicular directions. The swab was then immersed in 3 mL ethanol and mechanically agitated for 20 s to dissolve any substances transferred from the sample to the swab. This solution was analyzed directly to quantify DOTP and DOP, as well as transesterified to quantify ESBO.[25] The ethanol contained 5 ppm 1-ethyl naphthalene (1-EN) and 5 ppm dimethyl pimelate (DMPi) as internal standards. Three samples were tested for each time interval and were discarded after swabbing.

To analyze ESBO, the exudate solutions were derivatised using 21% sodium ethoxide/ethanol solution to

convert the triglyceride to ethyl esters. This allows for analysis of ESBO by GC–MS under standard conditions due to the increased volatility of the resulting ethyl esters compared with ESBO. The internal standard DMPi also undergoes transesterification in these conditions, and this is used to monitor the reaction. Sodium ethoxide solution can absorb moisture during storage which can lead to saponification of the esters. The concentration of diethyl pimelate (DEPi) produced from DMPi was monitored to identify any issues with the sodium ethoxide reagent.

1 mL of the ethanol solutions was added to 0.325 mL of sodium ethoxide/ethanol solution, shaken and allowed to react for 5 min. 2 mL MTBE/hexane (60/40%) and 2 mL disodium citrate solution was added. The organic phase was then separated and dried over excess magnesium sulfate and filtered using pipette filters (Fisherbrand, PTFE 0.2 μm) into vials for GC–MS analysis.

GC–MS analysis was carried out on an Agilent 7890B/5977B. 1 μL injection volume, inlet 300°C, splitless, 1 mL/min column flow helium. The column was an Agilent HP-5MS UI, length 30 m, ID 0.25 mm. 60–100°C at 7°C/min, then 15°C/min to 300°C, hold 5 min.

Samples of known concentration were prepared and used as calibration standards. A total of 6 concentration levels were prepared, and 3 repeats were tested. A quadratic fit was used, giving an $R^2$ value of 0.995 for DOTP and 0.996 for DOP. Method blank samples were prepared by immersing clean swabs in 3 mL ethanol containing the internal standard and were tested alongside the samples and standards. This confirmed that the swabs did not release any substances that would interfere with the results.

These standards were also derivatised as described to quantify ESBO. This gave rise to a number of peaks due to the mixed composition of the ESBO triglycerides. The peak corresponding to ethyl 9-epoxystearate (Et 9-ES) was chosen for quantification, giving an $R^2$ of 0.994 with a quadratic fit. This peak was chosen from four potential ESBO derivative peaks as it had sufficient intensity and no overlapping peaks – see Data S1.

## 3.5 | Dynamic mechanical analysis

DMA was used to investigate the low temperature properties of the samples. Samples were tested on a Perkin Elmer DMA8000 from −130 to 70°C at a rate of 5°C/min in tensile mode. The samples were exposed to an oscillating strain of 0.5 mm at a frequency of 1 Hz.

# 4 | RESULTS AND DISCUSSION

## 4.1 | Visual exudation evaluation

Samples were tested in the compatibility loop for 60 min, then removed and wiped with a dry test paper. The paper was examined for exudation visually in accordance with the ASTM D3291 standard. All samples showed no visible exudation, and so would be given a grading of 0 by the ASTM D3291 scale under these conditions.

## 4.2 | FT-IR spectroscopy

The FTIR carbonyl stretch peak position (1700–1800 cm$^{-1}$), can be used for qualitative identification of the different plasticisers used in this study (Figure 4). It is expected that interaction of the plasticizer with the PVC matrix will lead to a change in peak position depending on the change in bond properties, as shown in other works.[13–17] To that end, the peak positions for single plasticisers, plasticizer mixtures, the PVC compound samples prior to the loop compression test, and PVC samples after compression, were measured.

The carbonyl peak in the plasticizer shifts to a lower wavenumber, albeit small differences (1–4 wavenumbers) when in the PVC compound (Table 2). This could be ascribed to interactions with the C-Cl bonds in the polymer which weaken the carbonyl bond.[26]

The carbonyl peaks of the individual plasticisers in the plasticizer mixtures (either as free liquids (1:1 DOTP-ESBO and 1:1 DOP-ESBO) or in the PVC compound)
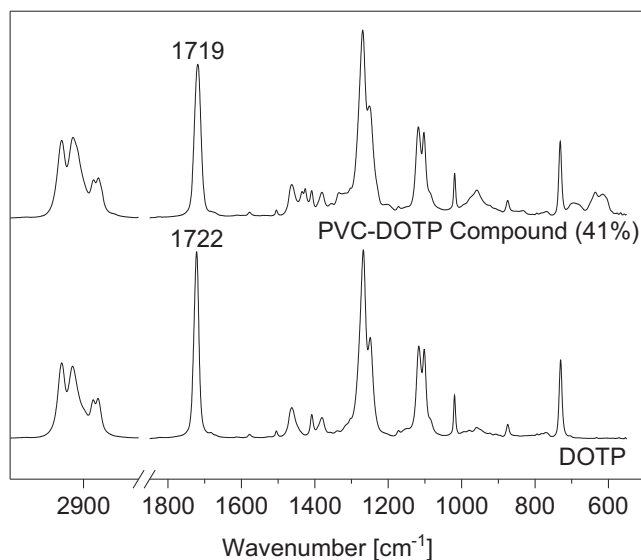


**FIGURE 4** FTIR spectra of DOTP and a DOTP-plasticised PVC sample (Formulation 1), with the carbonyl symmetric stretching band indicated.

**TABLE 2** Carbonyl peak positions of each plasticizer individually and in the mixtures (DOTP-ESBO) and (DOP-ESBO) investigated, with the difference from the single plasticizer in brackets.

| Plasticizer | DOTP carbonyl position (cm$^{-1}$) | DOP carbonyl position (cm$^{-1}$) | ESBO carbonyl position |
|---|---|---|---|
| Single plasticizer | 1722.5 | 1728.5 | 1742.4 |
| DOTP-ESBO mixture | 1720.7 ($-1.8$) | - | 1744.3 ($+1.9$) |
| DOP-ESBO mixture | - | 1724.8 ($-3.7$) | 1739.8 ($-2.6$) |

**TABLE 3** Carbonyl peak positions in PVC formulations, and shift in carbonyl peak position between the free plasticizer (or plasticizer mixtures for Formulations 4 and 5) and the plasticised PVC samples before compression testing.

| Sample | Carbonyl peak position (cm$^{-1}$) | Carbonyl shift relative to free plasticizer (cm$^{-1}$) |
|---|---|---|
| Formulation 1—DOTP | 1719.2 | $-3.4$ |
| Formulation 2—DOP | 1724.6 | $-4.0$ |
| Formulation 3—ESBO | 1739.9 | $-2.5$ |
| Formulation 4—DOTP | 1719.2 | $-1.6$ |
| Formulation 4—ESBO | 1742.0 | $-2.2$ |
| Formulation 5—DOP | 1723.0 | $-1.8$ |
| Formulation 5—ESBO | 1739.2 | $-0.6$ |

overlapped and therefore deconvolution was used to identify peak positions. The WIRE® software package of the Renishaw Invia Raman spectrometer was used to perform the deconvolution. The optimum deconvolution was achieved by manually providing boundaries for peak positions and a maximum of 3000 iterations, with a tolerance value of 0.001. The model provided a best fit using a mixture of Gaussian and Lorentzian peak shapes.

The peaks found by this method for the plasticizer mixtures were shifted relative to the single plasticisers, as shown in Table 2. These data suggest an interaction between the plasticisers in the mixtures leading to a change in the carbonyl bond energy following mixing. In DOTP and DOP individually, the carbonyl groups will interact most strongly with other carbonyl groups due to the electronegativity of the carbonyl oxygen. However, these groups are relatively sterically hindered by their position next to the aromatic ring, particularly so for DOP where the carbonyl groups are in the ortho position. ESBO contains epoxide groups in addition to ester groups, and these are located on long alkyl chains which are more mobile and may be more able to interact with the para- and ortho-phthalate ester groups. This explanation could explain the corresponding increase in the ESBO carbonyl position in the DOTP-ESBO mixture, if this interaction reduces the number of epoxide groups interacting with ESBO carbonyl groups. However, it

would not explain the negative shift of the ESBO carbonyl bond in the mixture with DOP.

The carbonyl peaks in all formulations tested showed a shift between the free plasticizer(s) and the plasticised PVC samples (Table 3). However, following 60 min compression, the carbonyl peak positions had not changed significantly relative to the resolution of the FTIR instrument. A change in peak position was predicted based on exuded plasticizer dominating the spectra. As the magnitude of the initial shift in carbonyl is already close to the resolution of the FTIR instrument, low levels of exudation such that the FTIR measurement is of a mixture of free and bound plasticizer is likely to be below the detection limit of the method.

The carbonyl shift in the PVC compound corresponds to the strength of the interaction between the PVC and the carbonyl group of the plasticizer.[13] By this measure, in the single plasticizer formulations DOP would be considered the most compatible (strongest interaction) and ESBO the least compatible (weakest interaction).

In Formulation 4 (PVC-DOTPESBO) the carbonyl shift at $t = 0$ was substantially smaller for DOTP ($-1.6$ cm$^{-1}$) compared to Formulation 1 (PVC-DOTP, $-3.4$ cm$^{-1}$), while the ESBO carbonyl shift was similar to that of Formulation 3 (PVC-ESBO). This would suggest that the compatibility of DOTP is reduced when mixed with ESBO. In Formulation 5 (PVC-DOPESBO) both DOP and ESBO $t = 0$ carbonyl shifts are significantly lower compared to each plasticizer alone. ESBO in particular changed by only 0.6 cm$^{-1}$. However, comparing the absolute carbonyl peak position gives a different picture. In Formulation 4 the DOTP peak has the same wavenumber as in Formulation 1 (1719.2 cm$^{-1}$) while the ESBO peak shows negligible shift relative to free ESBO (1742.0 and 1742.4 cm$^{-1}$). DOP is shifted to lower wavenumber in Formulation 5 compared with Formulation 2, while the ESBO peak position is similar to that of ESBO in Formulation 3.

The formulations chosen for this analysis were designed to simplify any analysis, containing only the PVC polymer, plasticisers, and a heat stabilizer. However, in typical PVC formulations, the use of FTIR analysis may be further complicated by the presence of the other components in the material. For example, Linde analyzed

**TABLE 4** Exuded plasticizer at t = 60 min measured by GC–MS quantification alongside the plasticizer composition of the tested PVC formulations.

| | Plasticizer composition in formulation (%) | | | Exudation (µg) | | |
|---|---|---|---|---|---|---|
| | DOTP | DOP | ESBO | DOTP | DOP | ESBO |
| Formulation 1—PVC-DOTP | 41.2% | | | 83.9 | - | - |
| Formulation 2—PVC-DOP | | 41.2% | | - | 7.6 | - |
| Formulation 3—PVC-ESBO | | | 41.2% | - | - | 9.8 |
| Formulation 4—PVC-DOTPESBO | 20.6% | | 20.6% | 14.5 | - | 8.0 |
| Formulation 5—PVC-DOPESBO | | 20.6% | 20.6% | - | 5.3 | 3.4 |

samples containing high levels of carbon black, which made IR analysis impossible due to the strong absorption.[27] Carbon black is relatively common in PVC formulations and so this would limit the method. A number of other common additives in PVC formulations contain carbonyl groups such as acrylic processing aids and copolymers such as vinyl acetate.[28] Calcium carbonate, which is widely used as a filler material in PVC formulation, shows a strong, broad feature in FTIR analysis centred at 1360 cm$^{-1}$ due to the asymmetric stretch in the $CO_3^{2-}$ anion.[29] Calcium carbonate was not used in the formulations tested in this work, however due to the prevalence within PVC formulations it should be considered in future work.

A further limitation of the ATR-FTIR method is that it requires good contact between the sample and the ATR crystal to obtain high quality data. The ATR attachment clamps the sample to the ATR crystal, ensuring close contact. This could be affecting the FTIR results, since the pressure applied by the ATR clamp could force the liquid plasticizer on the sample surface to flow away from the point of contact of the crystal. This would limit the amount of plasticizer that could accumulate between the solid PVC sample and the crystal, and so could potentially affect the accuracy of the results. Additionally, compatibility as measured by initial carbonyl shift may not directly correlate to the overall strength of the plasticizer-polymer solvation, as other parts of the plasticizer molecule may also interact with the polymer.

## 4.3 | GC–MS analysis

The compounds present in the swab extracts and derivatised samples were quantified using the Agilent MassHunter software. Each plasticizer was quantified by the ion with the highest response, and qualifier ions were chosen to validate the results. The intensity of the qualifier is compared to the quantifier to confirm that the correct target molecule is being measured. For DOTP, the
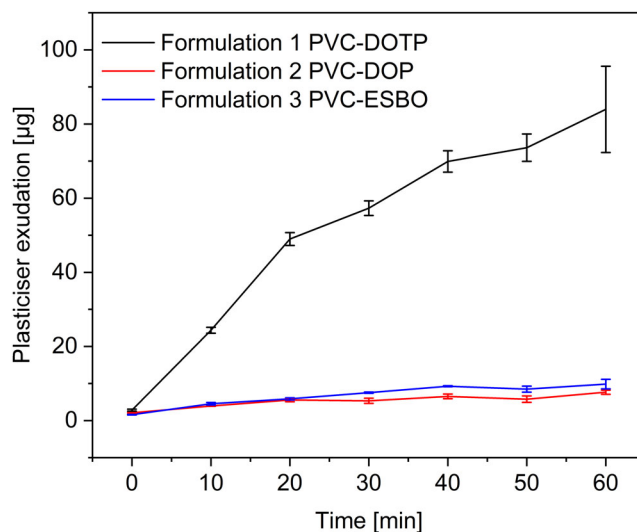


**FIGURE 5** Plasticizer exudation by GC–MS for PVC samples containing DOTP, DOP and ESBO, following compression in the 'loop spew test'. [Color figure can be viewed at wileyonlinelibrary.com]

quantifier ion had an m/z value 167, qualifier 261, and for DOP the quantifier ion had an m/z value 149, qualifier 167. For the representative peak for ESBO, Et9-ES, m/z 155 was chosen as quantifier and 69.1 as qualifier.

Table 4 shows the measured exuded plasticizer for each sample alongside the composition of the samples. As seen in Figure 5, DOTP (Formulation 1) gives the highest level of exudation of the single plasticizer samples – ten times more than DOP (Formulation 2) or ESBO (Formulation 3). The exudation appears to follow a non-linear pattern of a steep early gradient followed by a more gradual increase.

Figure 6 shows the exudation of plasticisers in the mixed plasticizer formulations, alongside the relevant single plasticizer formulation. The DOTP exuded from Formulation 4 was 17% of that exuded from Formulation 1, despite the concentration of DOTP in Formulation 4 being 50% of that in Formulation 1. This reduction in exudation contrasts with FTIR analysis, which suggested
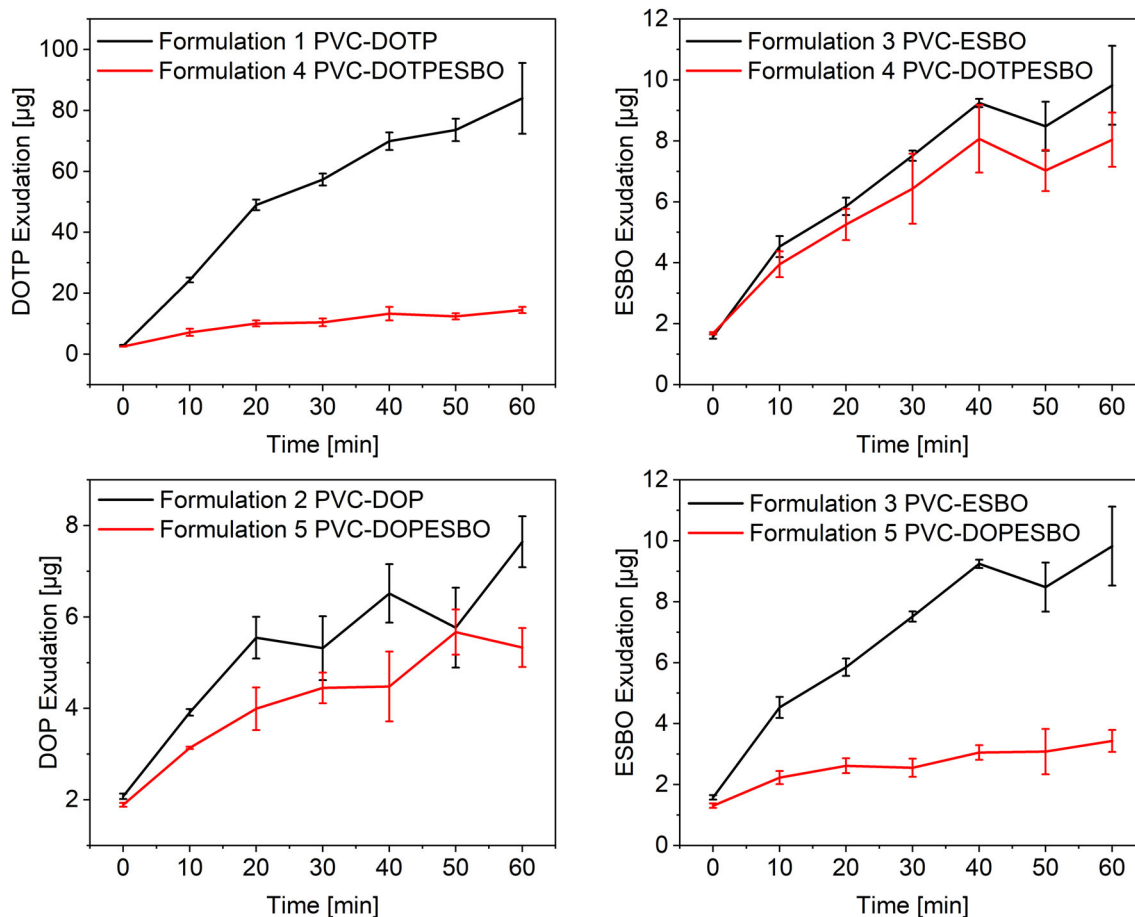
**FIGURE 6** Plasticizer exudation from the mixed plasticizer formulations (shown in red) alongside the exudation of the component plasticisers from the single plasticizer formulations (black) following compression in the 'loop spew test'. [Color figure can be viewed at wileyonlinelibrary.com]

that DOTP interacted less strongly with PVC when in a mixture with ESBO. Conversely, the mixture of plasticisers in Formulation 5 appears to increase the exudation of DOP and decrease the exudation of ESBO, relative to the concentration in the PVC sample. In fact, while ESBO exuded more rapidly than DOP in the single plasticizer Formulations 2 and 3, when mixed in Formulation 5 this was reversed, with DOP exuding faster than ESBO. The exudation of plasticizer was quantifiable for all samples tested by GC–MS, which highlights the increased sensitivity of the method.

In addition to quantifying the amount of plasticizer exuded from the PVC matrix, an attempt was also made to determine the kinetics of the exudation for the various plasticisers and combinations thereof. An example is illustrated in Figure 7 for DOTP, where the amount of plasticizer exuded over time was fitted to a first order process with a reasonable degree of success ($R^2 = 0.96$). The other plasticisers and combinations yielded poorer fits to both zero and first order processes. The various attempts
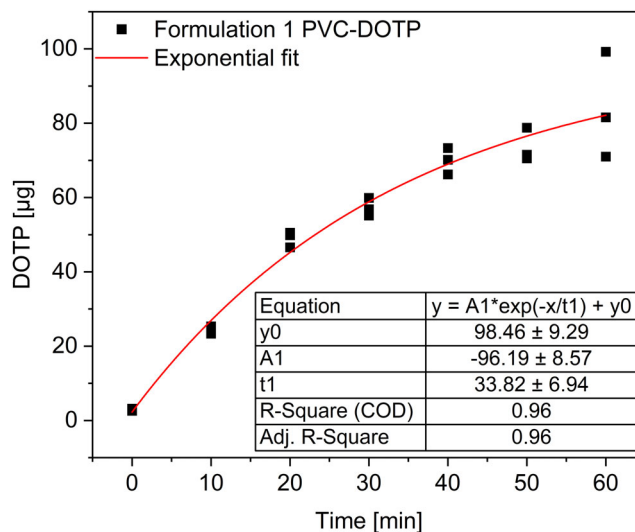


**FIGURE 7** Exponential fit of DOTP exudation from Formulation 1 by GC–MS. [Color figure can be viewed at wileyonlinelibrary.com]

**TABLE 5** $R^2$ values for exponential fits to the plasticizer exudation data as measured by GC–MS.

| Formulation | Plasticizer | Linear fit $R^2$ | Exponential fit $R^2$ |
| --- | --- | --- | --- |
| Formulation 1 | DOTP | 0.91 | 0.96 |
| Formulation 2 | DOP | 0.69 | 0.72 |
| Formulation 3 | ESBO | 0.84 | 0.92 |
| Formulation 4 | DOTP | 0.79 | 0.88 |
| Formulation 4 | ESBO | 0.76 | 0.85 |
| Formulation 5 | DOP | 0.79 | 0.85 |
| Formulation 5 | ESBO | 0.79 | 0.84 |



**FIGURE 8** An example of the storage modulus, loss modulus and tan delta data produced by DMA analysis. Measurements of glass transition temperature include the onset of Storage modulus (intersection of tangents) and peak of loss modulus as illustrated. [Color figure can be viewed at wileyonlinelibrary.com]

are summarized in Table 5 and illustrate that for all datasets, the exponential fit gives a higher $R^2$ than the linear fit.

The results obtained by GC–MS analysis show that this method can be used to quantify plasticizer exudation from PVC. In comparison with the ASTM D3291 standard method of a subjective rating of visible exudation on a 4-point scale, this method is based on an objective measurement and shows greatly improved sensitivity, as no exudation was visually observed within 60 min by the ASTM standard method. The plasticizer exudation results do not correlate strongly with the FTIR compatibility measurement of the weakening of the plasticizer carbonyl bonds. PVC-DOTP showed the highest level of plasticizer exudation by GC–MS, even though this formulation showed the second highest carbonyl peak shift by FTIR. This would suggest that exudation is controlled by other factors, such as interactions between other parts of the plasticizer molecule as well as kinetic factors.

The method of testing plasticizer exudation over time, as used for the GC–MS analysis, is very labour-intensive, and the variance in results was shown to be quite high in some cases. As all samples appeared to follow similar trends in exudation behavior, it could be beneficial to develop a test method based around a single compression interval.

## 4.4 | DMA analysis

The DMA data was used to produce plots of storage modulus, loss modulus and tan delta for the samples. These plots were examined to determine the glass transition temperature as well as any signs of phase separation which would indicate incompatibility. The storage modulus ($E'$) represents the elastic (glassy) component of the material while the loss modulus ($E''$) represents the inelastic (rubbery) component. As the sample temperature is
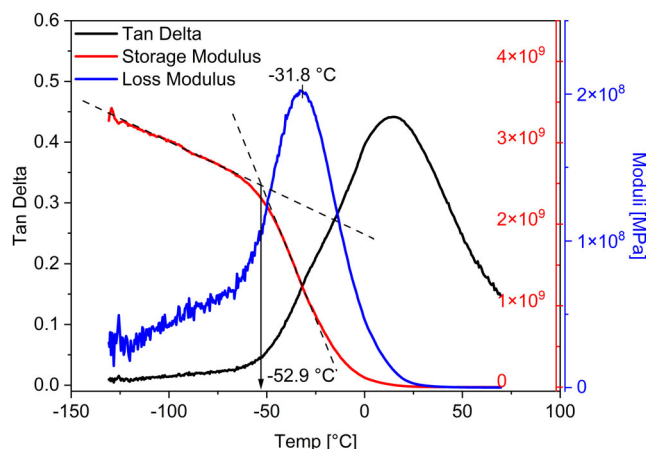
increased, the polymer changes from glassy behavior to rubbery behavior. The point at which this change occurs is the glass transition temperature. Storage and Loss modulus are related by the tan delta as calculated in Equation (1).

$$tan\delta = \frac{E''}{E'} \tag{1}$$

All samples showed similar overall trends in both storage and loss modulus, producing profiles such as the example shown in Figure 8. The samples gave a clear single glass transition temperature, which can be measured by either the onset of the storage modulus decrease, or the peak of the loss modulus curve. These data are presented in Table 6.

The storage modulus onset and loss modulus peak values both show the same trends between the plasticised samples – Formulation 1 (PVC-DOTP) and Formulation 2 (PVC-DOP) gave the lowest $T_g$ values, and Formulation 3 (PVC-ESBO) the highest, with the $T_g$ for the mixtures at approximately the midpoint of those values. This suggests that the ability of the individual plasticisers to solvate and lubricate the PVC chains is unchanged when combined in the mixtures tested. Additionally, no evidence of phase separation (that would indicate poor compatibility) was detected in any sample by DMA.

Table 7 summarizes the methods evaluated for plasticizer compatibility testing. It is clear that there is little correlation between the methods, besides PVC-DOP showing the greatest compatibility by both FTIR and GC–MS. While exudation behavior suggests that DOTP is less compatible than DOP, it is also more effective at

**TABLE 6** Glass transition temperatures (and standard deviations) measured by storage modulus onset and loss modulus peak, and the FTIR carbonyl peak shifts representing the strength of the interaction between carbonyl and the PVC C-Cl bonds.

| Sample | Storage modulus onset (°C) | Loss modulus peak (°C) | FTIR carbonyl peak shift (cm$^{-1}$) |
|---|---|---|---|
| Formulation 1—PVC-DOTP | −51.2 (0.2) | −32.7 (0.9) | −3.4 |
| Formulation 2—PVC-DOP | −47.3 (2.5) | −29.9 (0.7) | −4.0 |
| Formulation 3—PVC-ESBO | −29.8 (1.0) | −12.8 (0.3) | −2.5 |
| Formulation 4—PVC-DOTPESBO | −38.2 (1.1) | −22.3 (0.2) | −1.6/−2.2 |
| Formulation 5—PVC-DOPESBO | −38.0 (2.7) | −20.9 (0.8) | −1.8/−0.6 |

**TABLE 7** Summary of the outcomes for the four methods of compatibility testing – ASTM D3291, FTIR carbonyl shift, GC–MS of exudation and glass transition temperature by DMA.

| Compatibility measure | ASTM D3291 method | FTIR carbonyl shift | Exudation by GC–MS | Glass transition temperature |
|---|---|---|---|---|
| Most compatible | n.d. | DOP | DOP | DOTP |
| Least compatible | n.d. | DOP-ESBO | DOTP | ESBO |

reducing the glass transition temperature of the PVC, and so is classified as the most compatible by this measurement. This highlights the need to consider the way that compatibility is defined when developing new plasticisers for use in PVC, as clearly the glass transition behavior is only one aspect of the relationship between the polymer and plasticizer.

# 5 | CONCLUSIONS

Four methods of determining plasticizer compatibility in PVC have been evaluated and compared for PVC formulations containing three plasticisers individually and in combination. GC–MS was used to quantify the plasticizer exudation on the surface of plasticised PVC samples stressed as described in the ASTM D3291 compatibility test. This method was able to detect and quantify plasticizer exudation that was not visible by the ASTM D3291 standard method. DOP displayed greater resistance to exudation than DOTP, while the presence of ESBO in the formulations appeared to enhance DOP migration and decrease DOTP migration. Correspondingly, the presence of DOTP increased ESBO migration, while the presence of DOP reduced ESBO migration. By fitting the data, it was shown that the process of exudation likely follows first order kinetics, however this was not conclusive due to high variance in the data.

FTIR was used to determine the carbonyl peak shift in the PVC compound relative to the free plasticizer (or a representative mixture of plasticisers). This is considered to be a measure of the strength of the interaction of the carbonyl group with the PVC chain, and thus indicative of compatibility. Aside from DOP, which showed the greatest carbonyl peak shift and lowest exudation by GC–MS, minimal correlation was found between the FTIR and GC–MS results. An attempt was made to quantify plasticizer exudation using FTIR, but this method was found to have insufficient sensitivity for this application.

These results were compared with the glass transition temperatures of the materials, as measured by DMA. It was shown that the $T_g$ values do not correlate with the amount of exudation of the plasticisers – Samples 1 and 2, plasticised solely by DOTP and DOP respectively, had very similar $T_g$ values but showed very different amounts of exudation.

GC–MS was shown to be a potentially viable method of improving upon the current ASTM D3291 compatibility test, as it is highly sensitive, repeatable and is based on objective measurement as opposed to subjective classifications. While the other methods for evaluating plasticisers give further information about the interactions between PVC and plasticizers in these PVC compounds, they could not be used as an indication of the tendency of the plasticizer to exude. However, the methods in combination could give a more complete picture of the compatibility of the plasticisers in PVC.

## AUTHOR CONTRIBUTIONS
**Katharine Burns:** Conceptualization (lead); formal analysis (lead); investigation (lead); methodology (lead); writing – original draft (lead). **Johannes H Potgieter:** Conceptualization (supporting); supervision (lead); writing – review and editing (equal). **Sanja Potgieter-Vermaak:** Conceptualization (supporting); supervision (supporting);

writing – review and editing (equal). **Ian D. V. Ingram:** Supervision (supporting); writing – review and editing (equal). **Christopher M Liauw:** Investigation (supporting); supervision (supporting).

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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## SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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