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ARTICLE

The quantification of di-octyl terephthalate and calcium carbonate in polyvinyl chloride using Fourier transform-infrared and Raman spectroscopy

Kate S. Irvin[1] | **Johannes H. Potgieter**[1,2] | **Christopher Liauw**[3] | **Robert Sparkes**[1] | **Sanja Potgieter-Vermaak**[1,4]

[1]Department of Natural Sciences, Manchester Metropolitan University, Manchester, UK

[2]School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa

[3]School of Healthcare Sciences, Manchester Metropolitan University, Manchester, UK

[4]Molecular Science Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

Correspondence

Kate S. Irvin, Department of Natural Sciences, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, UK.

Email: kate.s.irvin@stu.mmu.ac.uk

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Abstract

The polyvinyl chloride (PVC) industry relies heavily on material property testing during the development of a product. Many of these testing procedures are outdated and time-consuming, resulting in high financial input. Non-destructive, fast, easy-to-use testing methods can significantly reduce the time required to quantify raw materials. We explored alternative analysis techniques, Fourier transform-infrared (FT-IR) and micro-Raman spectroscopy to quantify the main components within a plasticised PVC (pPVC) compound with dioctyl terephthalate (DOTP) plasticizer and calcium carbonate filler. This can reduce costs in the testing and development of new products up to 50%. We prepared 36 samples with varying proportions of DOTP and calcium carbonate and analyzed them using a Raman Microscope and FT-IR Spectrometer. We found a strong correlation ($R^2 = 0.923$) between DOTP and FT-IR spectroscopy data, as well as a strong correlation (FT-IR $R^2 = 0.910$; Raman $R^2 = 0.813$) between the calcium carbonate and data obtained with both spectroscopies. We reported for the first-time correlations that could be used to determine the raw material levels within pPVC provided by both techniques. Five samples were then made and tested, showing some success in the quantification. This study provided a solid baseline for reducing the time taken to make a recommendation from >168 h to <1 h and therefore reducing the costs of product development by up to 50%.

KEYWORDS

calcium carbonate, DOTP, FT-IR spectroscopy, poly vinylchloride, Raman spectroscopy, spectroscopy

1 | INTRODUCTION

Polyvinyl chloride (PVC) is the third most used polymer globally, due to its versatility and low production costs.[1] PVC compounds are used in many applications, including building and construction, medical devices, and cables.[2] Testing of any PVC product is typically completed during development, production (quality control [QC]), use (by customers of the end-product), and at the end of its life (when being recycled). The current

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TABLE 1 An outline of the common test methods used within the PVC industry, showing the relevant standards, PVC type, property, conditioning time, test time, instrument, main influencer, secondary influencer, skill level required and at what stage this would normally be performed

Performed during	Development QC	Development	Development QC	Development QC	Development	Development QC	Development	Development	Development	Development
Skill level required	Low	Low	Low	Low	Medium	Medium	Low	Medium	Medium	Medium
Secondary influencer	Filler	Filler	Plasticizer	Some plasticisers	PVC type	Filler	Stabilizer package	Stabilizer package	Filler	Filler and plasticizer level
Main influencer	Plasticizer	Plasticizer	Filler	Stabilizer package	Plasticizer/ filler	Stabilizer package/ plasticizer	PVC type	Plasticizer/ PVC type	Stabilizer package/ PVC type/ plasticizer	Flame retardant additives
Instrument	Softness meter	Hardness meter	Density balance	Heated block	Tensometer	Extruder	Vicat tester	Melt flow rheometer	Mixing head rheometer	LOI
Test time (hours)	1	1	0.5	0.5–10	1	1	2	1	1	1
Conditioning time (hours)	168	168	1	N/A	24	N/A	24	N/A	N/A	36
Property	Material softness	Material hardness	Relative density	Heat stability	Tensile strength, elongation	Pressure, torque, melt temp. Surface finish	Softening point of the material	Flow of the material	Gelation time and fusion properties	Flame retardance
PVC type	pPVC	pPVC	Both	Both	Mainly pPVC	Both	uPVC	Both	Mainly uPVC	Both
Standard (if applicable)	BS 2782–3: 365A (1976)	BS EN ISO 868 (2003)	BS 2782–6: 620A– 620D (1991)	BS 2782–1: 130A (1991)	BS 2782–3: 320A– 320F (1976)	N/A	BS EN ISO 306 (2013	BS EN ISO 1133: 1 (2011)	N/A	BS EN ISO 4589: 2 (1999)
Test	British standard softness	Shore A hardness	Relative density	Congo red test	Tensile testing	Extrusion	Vicat softening point	Melt flow rheology	Mixing head rheometry	Limiting oxygen index

Abbreviations: PVC, polyvinyl chloride; pPVC, plasticised PVC; QC, quality control; uPVC, unplasticized PVC.

methods of testing, including British Standard Softness and tensile properties, are often outdated, inefficient, and require prior knowledge of the PVC compound (see Table 1 for a full list of testing procedures). In addition, changes to legislation in recent years have regulated the type and level of additives that can be used within a PVC compound.[3,4] The industry faces worldwide pressure from consumers and governments to reduce plastic waste.[5] Therefore, now more than ever, the PVC industry should invest in continuous assessment and development of reliable, stringent test methods to ensure fast and accurate testing of compounded PVC and its many properties.[6,7] The two main events during which PVC compound evaluation will occur, are during product development and QC testing during material production. Both testing events play a crucial role and are essential to maintain a healthy circular economy in the industry.[8] Product development, to either new or existing specifications, requires several test procedures, as outlined in Table 1. During the production stage QC testing will be required, which would generally consist of a lower level of testing. The nature of these tests in both cases will depend on whether the material is a plasticised PVC (pPVC) compound or an unplasticized PVC (uPVC) compound.[9] The tests completed, within the industry, are normally physical tests, which can be labour intensive and time consuming, as well as requiring prior knowledge of PVC compounds and their behavior.

Table 1 outlines several tests that may be performed within industry, giving time scales, as well as the relative skill level required. Many of the tests are also used within academic research, however there is generally a higher focus on more advance testing, such as spectroscopic techniques, thermal analysis, and surface analysis.[10,11] Testing is often time consuming, involving up to 168 h (7 days) of conditioning time for some of the tests required during the development and QC stages. With the current testing regime, a minimum of 14 days is being lost solely to conditioning time. Whilst the conditioning time does not require manpower, its financial impact lies in the delay of a market-ready product. If this time loss could be eradicated this would no doubt have a huge impact on the industry. It is evident that if an alternative test procedure could provide the same information as the testing outlined in Table 1 in a shorter timeframe, profits could be reaped much earlier, and problems resolved much quicker.

It is well documented that two of the most influential raw materials in PVC compounds are plasticisers and fillers. Plasticisers are used to soften PVC compounds at room temperature. Normal softening points are >70°C. One of the most used commercial plasticisers, is dioctyl terephthalate (DOTP). DOTP is a general-purpose plasticizer, with the added advantage that it is considered "phthalate free" within the plastic industry, meaning that it does not contain ortho-phthalates and therefore is not restricted in its use.[12,13] The role of filler on the other hand is, generally, to produce the material at a lower cost, though it can sometimes offer additional properties. The most common type of filler is calcium carbonate, as it is inexpensive, consistent, and readily available. It is also available in many different grades, making it more versatile than many other fillers.[14,15] As well as PVC resin, all PVC compounds will contain a stabilizer package. This is normally a combination of multiple metal soaps which are used to ensure that the material does not degrade, rendering it useless.[16]

Table 1 outlines not only the tests and test durations, but the raw materials that have the largest influence on the properties being tested. Whilst there are some properties, which are very particular and may require special additives, for pPVC the two biggest influencers are plasticizer and filler, due to the flexibility requirement of the end-product. When completing development work within the PVC industry it is crucial to be able to assess the levels of both plasticizer and filler present within a pPVC compound. There are various ways to do this, however currently it is still extremely common for the raw material levels to be predicted from the physical properties, such as British Standard Softness (BSS) and relative density.[9] Whilst other methods can be used, such as GC–MS (for plasticisers) and ICP-OES (for fillers), these are expensive and require a high skill level to run and interpret. These methods also require a lot of method development to extract/digest samples, as well as requiring chemicals that are not only hazardous under GHS, but also not "green".[17,18]

Within the PVC industry, FT-IR and other techniques are already utilized for the identification of individual components. With more companies creating combined FT-IR and Raman instruments, as well as handheld instruments becoming more widely available, it is likely that Raman analysis will be more frequently used within the industry in future.[19–21] These non-destructive techniques can only add true value to the PVC formulations process if they can provide quantitative data. Although there is evidence in literature of quantification using both these spectroscopic techniques, these refer to application in niche markets such as medical devices and food films[19,22] However, no reports could be found that simultaneously quantified the plasticizer and filler content of general-purpose PVC compound. Reliable quantitative analysis using these techniques requires robust method development and the production of in-house spectral databases. The lack of databases is one reason why these techniques are not currently widely used for PVC testing.

Furthermore, there are no green, or cost and time efficient ways to determine the plasticizer and filler content of a compounded PVC sample. Within the literature there have been several studies, which provide methods for quantification of raw materials within PVC compounds.[23,24] However, these often take a day to complete and frequently use equipment or methods either not readily available within the industry, as well as the use of hazardous solvents or acids, that are ultimately not good for the environment. What's more, the quantification of calcium carbonate by spectroscopic techniques has not been previously reported in PVC compounds. The current study aims to develop a method that allows spectroscopic techniques to be used to not only identify, but also quantify both the DOTP plasticizer and calcium carbonate filler levels present within a PVC compound. This could pave the way for a quick, green, cost-effective solution for raw material identification and quantification within the PVC industry.

2 | EXPERIMENTAL PROCEDURES AND MATERIALS

The quantification of calcium carbonate filler and DOTP plasticizer, and their interactions, within PVC compounds using spectroscopic techniques, require careful consideration of several variables. To investigate the use of spectroscopic techniques for the quantification of DOTP and calcium carbonate within compounded PVC, 36 formulations were produced. These formulations, outlined in Table S1, contain varying levels of PVC, DOTP, calcium carbonate and a calcium/zinc-based stabilizer package. The formulations were set up using “per hundred resin” (PHR) as this is the industry standard for PVC. Per hundred resin means that all raw materials are weighed out as a ratio again the PVC resin within the formulation, for example five PHR stabilizer would mean that there are five parts of stabilizer per 100 parts of resin. The PHR system allows for any units to be used due to it simply being a ratio. The formulations outlined in Table S1, the PVC and stabilizer package were kept at the same ratio within all the formulations (100:2.25). The raw materials selected for use were K70 PVC suspension resin (the standard PVC resin used for pPVC), DOTP plasticizer, calcium carbonate filler and a general-purpose calcium/zinc-based stabilizer package.

2.1 | Sample preparation

Thirty-six formulations were prepared, outlined in Table S1, using a 6″ × 13″ Farrell Two-Roll Mill (roll temperature: 155–160°C; roll speed front/back: 25.5 RPM/34.0 RPM). The samples were roughly hand mixed before being blended on the two-roll mill for 6 min, with crosscut and fold back being performed every 10 s throughout this process. The produced hide was then place on a stainless-steel sheet to cool. As the milled hide produces an uneven surface and thickness across the samples, the samples were molded to 2 mm on a Neoplast HYD 30 T press (platen temperature: 170°C; heating cycle: 5 min; cooling cycle: 8 min). Test pieces of an appropriate size were then cut using a RayRan compressed air sample cutting tool.

2.2 | Spectroscopic techniques

The samples were tested using a micro-Raman spectrometer and attenuated total reflection (ATR)-FT-IR spectrometer.

2.2.1 | Raman spectroscopy

All Raman spectroscopic testing was completed using a Thermo Scientific DXR Raman Microscope. A 532 nm laser was found to produce satisfactory results, with 900 lines/mm grating, 25 μm pinhole spectrograph aperture. The spatial resolution is estimated to be 2.7–4.2 cm^{-1}. After comparing ×10, ×25 and ×50 objectives, it was found that the ×10 lens gave the most representative results, with lowest variation. For each test 50 exposures were completed with an exposure time of 5 s.

2.2.2 | ATR-FT-IR spectroscopy

Spot tests were carried out on a Thermo Scientific Nicolet iS5 FT-IR Spectroscope with an iD5 ATR Diamond accessory. For each test 32 scans were completed, with a spectral resolution of 4 cm^{-1}, which was found to give suitable spectra. ATR (attenuated total reflection)-correction was used on all samples as standard.

2.3 | X-Ray diffraction

X-ray diffraction data were collected on a PANalytical X'pert Powder X-ray diffractometer using Cu Kα radiation ($\lambda = 0.51054$ Å) with generator settings of 45 kV, 40 mA. Automatic divergence and antiscatter slits were used on the incident and diffracted beam paths with data collected using a PIXCel 1-D detector operating in scanning line mode with an active length of 3.347° 2θ. The incident beam was passed through a 10 mm beam mask with the automatic divergence slits on the source set to maintain a

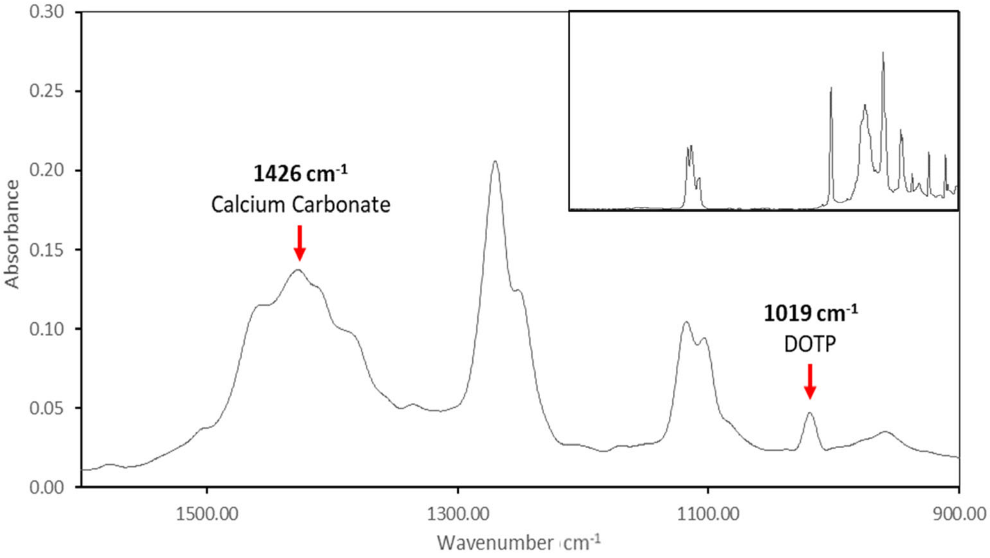

FIGURE 1 Figure showing an example Fourier transform-infrared (FT-IR) spectrum for plasticised PVC (pPVC) (top, right-hand corner) and the peaks for chosen for dioctyl terephthalate (DOTP) (1019 cm^{-1}) and calcium carbonate (1426 cm^{-1}) [Color figure can be viewed at wileyonlinelibrary.com]

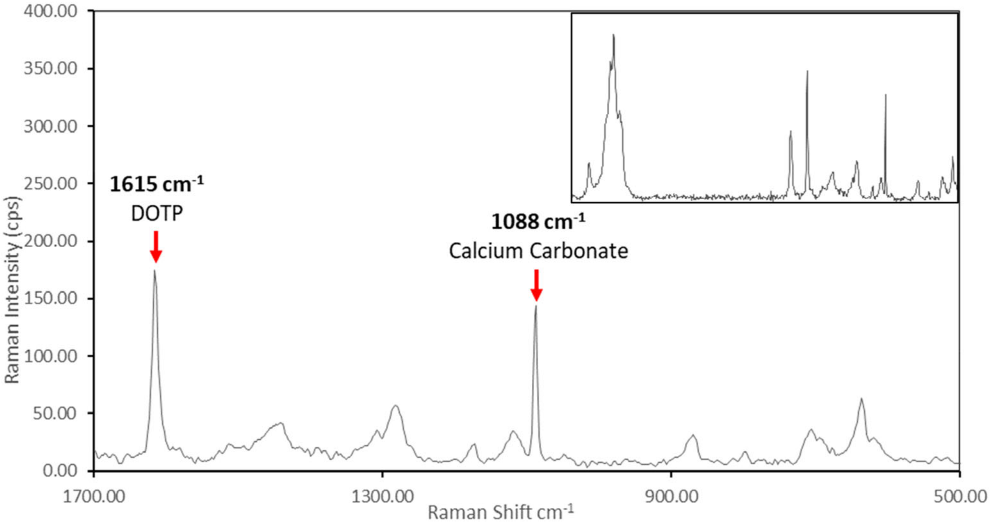

FIGURE 2 Figure showing an example Raman spectrum for plasticised PVC (pPVC) (top, right-hand corner) and the peaks for chosen for dioctyl terephthalate (DOTP) (1615 cm^{-1}) and calcium carbonate (1088 cm^{-1}) [Color figure can be viewed at wileyonlinelibrary.com]

constant irradiated length of 5 mm throughout the scan. The automatic anti-scatter slits on the detector were also set to maintain constant 5 mm aperture. Data were collected in the range 10–140° 2θ with a step size of 0.013° 2θ and a measuring time of 89 s/step. The samples were rotated at 60 rpm during the data collection. Data was truncated to the range 6–130° 2θ and converted to fixed divergence slit. The data was corrected for sample height errors using the expected peak positions for calcite.

3 | RESULTS AND DISCUSSION

3.1 | Spectroscopic techniques

For both FT-IR and Raman spectroscopy spot testing was completed in 10 separate spots on each sample, with multiple repeats being completed on each of these spots. An example of the spectra achieved for FT-IR can be seen in Figure 1 (inserted right-hand corner), the main figure shows the peaks identified for use for DOTP and calcium carbonate. Figure 2 shows an example spectrum for Raman spectroscopy (inserted right-hand corner), with identifying the peaks chosen for DOTP and calcium carbonate demonstrated in the main image. The average was then taken using the Omnic software to produce the spectra used. These spectra were then deconvoluted on Origin 8 software to determine the peak areas for relevant peaks, displayed in Figures 1 and 2. The peak areas were correlated with relevant raw material levels within the formulations for quantification purposes.

3.1.1 | DOTP plasticizer

Based on the criteria set out previously, for FT-IR analysis, the aromatic C—H in-plane bending peak at 1019 cm^{-1} (marked in Figure 1) was chosen to quantify

TABLE 2 Table outlining the trend line equations and R^2 values for the DOTP level (PHR) (y axis) versus the FT-IR and Raman spectroscopy peak areas at 1019 and 1615 cm^{-1} (x axis), respectively

PVC sample with DOTP levels (20, 40, 60, 80, 100 PHR) and various fixed amounts of $CaCO_3$ (0–100 PHR)	Trend line equation	Trend line R^2 value
FT-IR spectroscopy		
0 $CaCO_3$	$y = 0.0015x + 0.072$	0.984
20 $CaCO_3$	$y = 0.0016x + 0.057$	0.967
40 $CaCO_3$	$y = 0.0016x + 0.055$	0.965
60 $CaCO_3$	$y = 0.0014x + 0.057$	0.959
80 $CaCO_3$	$y = 0.0016x + 0.042$	0.946
100 $CaCO_3$	$y = 0.0015x + 0.046$	0.964
Average	N/A	0.964
SD	N/A	0.012
RSD (%)	N/A	1.278
All data	$y = 0.0015x + 0.055$	0.930
Raman spectroscopy		
0 $CaCO_3$	$y = 50.372x + 1474.1$	0.993
20 $CaCO_3$	$y = 23.512x + 754.1$	0.930
40 $CaCO_3$	$y = 15.368x + 599.1$	0.879
60 $CaCO_3$	$y = 24.719x + 475.2$	0.935
80 $CaCO_3$	$y = 17.954x + 185.1$	0.968
100 $CaCO_3$	$y = 12.322x + 339.58$	0.927
Average	N/A	0.939
SD	N/A	0.039
RSD (%)	N/A	4.153
All data	$y = 24.041x + 637.9$	0.241

Note: Divided into varying levels of calcium carbonate in PHR. Based on Figures S1 and S2.
Abbreviations: DOTP, dioctyl terephthalate; FT-IR, Fourier transform-infrared; PHR, per hundred resin; PVC, polyvinyl chloride; RSD, relative standard deviation.

the DOTP.[25] For the Raman spectroscopy the peak at 1615 cm^{-1} (in the aryl C—C stretch) (marked in Figure 2) was selected for the quantification of DOTP.[26] These peak areas were plotted against 20–100 PHR DOTP.

Table 2 shows the relationship between the DOTP PHR level and the peak areas for FT-IR spectroscopy (1019 cm^{-1}) and Raman spectroscopy (1615 cm^{-1}), grouped by the PHR level of the calcium carbonate and overall data set.

When using FT-IR, the trendlines found at each calcium carbonate level are all the same magnitude with similar intercepts, additionally the R^2 values found have a relative standard deviation (RSD) of only 1.28%. The trend line for "All Data" gives an R^2 value of 0.930, which suggests that there is a strong linear relationship between the DOTP level in the material and the peak area measured. The high R^2 value for "All Data", shows that the proportion of calcium carbonate filler had no significant influence on the linear regression. It would therefore be possible to predict DOTP levels using FT-IR data independent from the calcium carbonate level present in the sample.

When using Raman spectroscopy, the data shows that when the sample does not have calcium carbonate filler present, it gives a much higher peak area at 1615 cm^{-1} than when there is calcium carbonate present. This difference is not unexpected, because the addition of calcium carbonate to compounded PVC has previously been shown to decrease the crystallinity of PVC.[27,28] This difference in crystallinity is significant as materials which are more crystalline give stronger, sharper Raman peaks than their more amorphous counterparts.[29–31] At a level of 20 PHR calcium carbonate filler, the peak area is approximately half of that observed for the equivalent sample with no calcium carbonate filler. The trend line data shows that each individual line has a reasonably strong correlation, with an average R^2 value of 0.939, and a standard deviation of 0.04. However, the R^2 value for "All data", where samples with the same amount of DOTP, but variable amounts of $CaCO_3$ are grouped together, is only 0.241. Unlike the FT-IR data, the trend line equations from Raman spectroscopy demonstrate significant variation in the gradient. Therefore, calculations of DOTP levels using Raman data are affected by the calcium carbonate levels. This becomes more evident when a Pearson's correlation is done on the calcium carbonate level versus the gradient and intercept values of -0.769 and -0.882, respectively. This shows that there is a strong correlation between the trend lines and the individual calcium carbonate levels used to divide the data, therefore showing an influence of the calcium carbonate level on the results found.

Table 3 shows the results for DOTP normalized to percentage. The results were normalized to percentage to determine whether there were any further relationships, which could not be observed between the samples when using PHR.

For FT-IR spectroscopy, the trendline for "All Data" demonstrates that there is a reasonably strong linear relationship, with an R^2 value of 0.923. This is very similar with that found in Table 2, before the results were normalized to percentage. The results seen when using percentage give a better correlation when considering each individual calcium carbonate level, yielding an average R^2 value of 0.992, and a RSD of 0.62%. The trend line

TABLE 3 Table outlining the trend line equations and R^2 values for the DOTP level (y-axis) versus the FT-IR and Raman spectroscopy peak areas at 1019 and 1615 cm^{-1} (x axis), respectively, normalized to percentage

PVC sample with DOTP levels (normalized to %) and various fixed amounts of $CaCO_3$ (0–100 PHR)	Trend line equation	Trend line R^2 value
FT-IR spectroscopy		
0 $CaCO_3$	$y = 0.0035x + 0.036$	0.998
20 $CaCO_3$	$y = 0.0042x + 0.022$	0.997
40 $CaCO_3$	$y = 0.0045x + 0.024$	0.995
60 $CaCO_3$	$y = 0.0043x + 0.033$	0.990
80 $CaCO_3$	$y = 0.0051x + 0.017$	0.982
100 $CaCO_3$	$y = 0.0051x + 0.025$	0.988
Average	N/A	0.992
SD	N/A	0.006
RSD (%)	N/A	0.621
All data	$y = 0.0039x + 0.0382$	0.923
Raman spectroscopy		
0 $CaCO_3$	$y = 120.92x + 269.06$	0.982
20 $CaCO_3$	$y = 62.29x + 219.23$	0.979
40 $CaCO_3$	$y = 46.68x + 317.84$	0.936
60 $CaCO_3$	$y = 69.86x - 14.96$	0.980
80 $CaCO_3$	$y = 56.47 - 77.21$	0.977
100 $CaCO_3$	$y = 41.01x + 178.27$	0.932
Average	N/A	0.964
SD	N/A	0.024
RSD (%)	N/A	2.446
All data	$y = 97.90x - 626.74$	0.606

Note: Divided into varying levels of calcium carbonate in PHR. Based on Figures S3 and S4.

Abbreviations: DOTP, dioctyl terephthalate; FT-IR, Fourier transform-infrared; PHR, per hundred resin; PVC, polyvinyl chloride.

equations again show that all the gradients are of the same magnitude, though there is an obvious pattern not observed within the PHR data, with the gradient increasing with the calcium carbonate level. This can be further demonstrated when considering the Pearson's correlation, which gives a value of 0.926 for the gradients found for each calcium carbonate level. In the case of PHR this value was −0.131.

When using Raman spectroscopy, the samples with no calcium carbonate show peak areas which are much higher than the rest. The overall correlation, of All Data containing the whole data set, is higher than seen in Table 2, with an R^2 value of 0.606. However, it can still not be considered as evidence of a useful relationship. Individually, each calcium carbonate level does demonstrate a strong correlation with an average R^2 of 0.964, and a RSD of 2.45%. The trend line equations for the Raman data show that there is less variation in the trendlines between the samples containing calcium carbonate when compared with the equation for the case that do not contain calcium carbonate. Despite this, when looking at the Pearson correlation for the gradient versus the calcium carbonate PHR level a correlation of −0.73 was obtained, suggesting that the gradients do correlate with the calcium carbonate level.

When considering DOTP a better correlation was observed using FT-IR than when using Raman spectroscopy, for both PHR and percentage. The R^2 values were almost identical between both sets of results found when using FT-IR. The Raman results without the presence of calcium carbonate give results significantly different to those found when considering the samples containing calcium carbonate. There is a significant difference between the R^2 values found for the Raman when compared to the FT-IR. This is very evident when considering PHR: the difference is 0.689 and when using the percentage values the difference more than halves to 0.317. Despite this, the results found from Raman spectroscopy could also be useful, if it was first determined whether calcium carbonate filler was present within the sample. If Raman spectroscopy was to be used for predicting the DOTP level, in samples containing calcium carbonate filler, it would be advisable to use only the graph based upon the % as the variation in the PHR trend line would provide a much wider range of error.

3.1.2 | Calcium carbonate filler

For the quantification of calcium carbonate using FT-IR spectroscopy, the peak at 1426 cm^{-1} (marked in Figure 1). This peak is the result of $_3$ asymmetric CO_3 stretching from the carbonate ion.[32] The peak selected in this study for the quantification of calcium carbonate using Raman spectroscopy, is the peak located at 1088 cm^{-1} (marked in Figure 2). This peak is the result of the multiple C—O stretches within the calcium carbonate.[32]

These peak areas were plotted against the calcium carbonate level within each formulation, with the results at zero PHR calcium carbonate being removed. Within a practical application one would be able to determine whether the calcium carbonate was present or not by the presence or absence of the peak within the spectra. Calcium carbonate levels above zero PHR but

TABLE 4 Table outlining the trend line equations and R^2 values for the calcium carbonate level (PHR) (y axis) versus the FT-IR and Raman spectroscopy peak areas at 1436 and 1088 cm^{-1} (x axis), respectively

PVC sample with CaCO3 levels (20, 40, 60, 80, 100 PHR) and various fixed amounts of DOTP (0–100 PHR)	Trend line equation	Trend line R^2 value
FT-IR spectroscopy		
20 PHR DOTP	$y = 0.009x + 0.248$	0.979
40 PHR DOTP	$y = 0.008x + 0.169$	0.995
60 PHR DOTP	$y = 0.007x + 0.143$	0.988
80 PHR DOTP	$y = 0.006x + 0.125$	0.994
100 PHR DOTP	$y = 0.005x + 0.089$	0.996
Average	N/A	0.990
SD	N/A	0.007
RSD (%)	N/A	0.716
All data	$y = 0.007x + 0.155$	0.661
Raman spectroscopy		
20 PHR DOTP	$y = 1.853x + 88.235$	0.841
40 PHR DOTP	$y = 1.060x + 105.230$	0.769
60 PHR DOTP	$y = 1.330x + 63.679$	0.906
80 PHR DOTP	$y = 1.922x + 26.891$	0.819
100 PHR DOTP	$y = 1.685x + 31.411$	0.955
Average	N/A	0.858
SD	N/A	0.073
RSD (%)	N/A	8.534
All data	$y = 1.570x + 63.089$	0.661

Note: Divided into varying levels of DOTP in PHR. Based on Figures S5 and S6.

Abbreviations: DOTP, dioctyl terephthalate; FT-IR, Fourier transform-infrared; PHR, per hundred resin; PVC, polyvinyl chloride.

below 20 PHR are uncommon within pPVC and therefore extrapolation could be used beyond this point if the circumstances called for it. The removal of the samples at zero PHR calcium carbonate allowed a more useful linear correlation to be produced. As a material of this type with a DOTP level of zero PHR would not be made commercially, this level was also removed from the calcium carbonate data.

Table 4 shows the trend line equations and the R^2 values obtained from the calcium carbonate PHR level versus the peak areas for FT-IR spectroscopy (1426 cm^{-1}) and Raman spectroscopy (1088 cm^{-1}), grouped by the PHR level of the calcium carbonate and overall.

For “All Data” the FT-IR gives an R^2 value of 0.673, this suggest that there is a correlation which exists between all the data points, but that there is quite a large amount of variation. The individual DOTP levels show strong correlations, with an average R^2 value of 0.990 and an RSD of 0.72%. The trend line equations show that the gradients of the lines are similar. Both the gradient and intercept show a relationship indicating that as the DOTP level increases, the value of the gradient and intercept decrease. This is demonstrated by the Pearson's correlation of the DOTP level versus the gradient and the intercept, giving values or −1.000 and −0.969, respectively. This shows that there is a strong correlation between the DOTP level and the trend lines.

When using Raman spectroscopy, the trend line data for “All Data” gave an R^2 value of 0.603, close to that found when using FT-IR. This shows that there is a correlation present, however it is not strong and is unlikely to provide any good prediction for the calcium carbonate level within PVC. The average R^2 value for the individual DOTP levels is 0.858, with an RSD of 8.534%. Overall, the individual trend lines R^2 values show good linear correlations. The trend line equations show that the results are all the same magnitude, but that there is variation in the intercepts. This explains why the trendline for “All Data” is relatively low. Unlike with the results found for the FT-IR, the intercepts for the linear relationships using the Raman data do not show a clear pattern, though those with a lower DOTP level do appear to have higher intercepts, matching the same observation in the case of the FT-IR data. When looking at the Pearson's correlation between the DOTP level used and the intercept, a value of −0.883 is found.

The results were normalized to percentage to determine whether there were any further relationships which could not be observed when considering the PHR – and therefore not considering the overall varying levels in the raw materials that are not being investigated.

Table 5 shows that for FT-IR data the trendline for “All Data” has an R^2 value of 0.910. This suggests that when the data is normalized that there is a good linear correlation between the peak area and calcium carbonate level. The RSD is higher at 1.3%, which suggests that there is slightly more variation in the individual trendline correlations once they are normalized. The trend line equations are all the same magnitude, and as expected based on the overall R^2 value, the gradients are also relatively similar. When looking at the gradients for percentage, compared to PHR, they do not correspond to such a strict pattern, however, still show a general trend of higher intercepts with the lower PHR values. For the FT-IR is can be seen that the Pearson correlations decrease when using percentage rather than PHR values, dropping to −0.944 for the gradients and −0.666 for the intercepts. This suggests that the DOTP level has a lesser influence on the trend line when using percentage-based data. This could contribute to the increase in the R^2 value observed.

TABLE 5 Table outlining the trend line equations and R^2 values for the calcium carbonate level (y axis) versus the FT-IR and Raman spectroscopy peak areas at 1436 and 1088 cm^{-1} (x axis), respectively normalized to percentage

PVC sample with $CaCO_3$ levels (normalized to %) and various fixed amounts of DOTP (0–100 PHR)	Trend line equation	Trend line R^2 value
FT-IR spectroscopy		
20 PHR DOTP	$y = 0.023x + 0.068$	0.967
40 PHR DOTP	$y = 0.023x + 0.026$	0.977
60 PHR DOTP	$y = 0.020x + 0.034$	0.986
80 PHR DOTP	$y = 0.018x + 0.043$	0.998
100 PHR DOTP	$y = 0.018x + 0.020$	0.995
Average	N/A	0.985
SD	N/A	0.013
RSD (%)	N/A	1.302
All data	$y = 0.0023x - 0.020$	0.910
Raman spectroscopy		
20 PHR DOTP	$y = 4.965x + 44.321$	0.905
40 PHR DOTP	$y = 2.898x + 86.967$	0.754
60 PHR DOTP	$y = 3.854x + 44.125$	0.878
80 PHR DOTP	$y = 5.830x + 3.913$	0.769
100 PHR DOTP	$y = 5.636x + 8.718$	0.970
Average	N/A	0.855
SD	N/A	0.092
RSD (%)	N/A	10.757
All data	$y = 4.806x + 31.425$	0.813

Note: Divided into varying levels of DOTP in PHR. Based on Figures S7 and S8.
Abbreviations: DOTP, dioctyl terephthalate; FT-IR, Fourier transform-infrared; PHR, per hundred resin; PVC, polyvinyl chloride.

The Raman spectroscopy trendline for “All Data” in Table 5 gives an R^2 value of 0.813. As with the FT-IR data, this suggests that there is a good correlation within the data. For each individual trend line, the R^2 values are good, though there are some lower ones when compared with the corresponding FT-IR values. This is reflected in the average found, 0.855, with a RSD of 10.76%. Again, normalizing the data to percentage values gave a higher RSD value, showing that there is more variation between each DOTP level's R^2 value. The trend line equations show that the gradients are of the same magnitude, but there is quite a significant difference in the intercepts. This further demonstrates the variation between the samples.

When considering the calcium carbonate levels against the peak areas both techniques give good correlations for all the data. If it were to be a split into the individual DOTP levels, then the FT-IR demonstrates that it is a slightly better quantification technique to use. For calcium carbonate it is recommended that normalization is completed as this significantly improved the “All Data” R^2 values found for each technique, increasing by 31.9% for FT-IR and 28.6% for Raman spectroscopy.

3.2 | X-Ray diffraction

Ten samples were tested for their calcite level on XRD, the results found were then graphed against the calcium carbonate level in the material as seen in Figure 3 below. This gave a R^2 value of 0.925, showing that there is a strong correlation, providing further evidence of the calcium carbonate levels.

3.3 | Quantification trial

To test the viability of the correlations found for quantification of both the DOTP and calcium carbonate an additional five samples were produced using the same method that was used for the 36 samples already tested. The composition of these samples can be found in Table 6.

These five samples were tested using both the spectroscopic previously outlined. The resulting spectra from these samples were deconvoluted using Origin 8 and the areas for the relevant peaks can be found in Table 6. Due to the low R^2 squared value found for DOTP when using Raman spectroscopy this was not completed at this stage.

The results shown in Table 6 demonstrate that the theoretical results are relatively close to the actual results, with all being within 6.5 points of the actual value. The results found from DOTP are the most successful, with all being within 3.5 points of the actual value. Both the spectroscopic techniques provide similar differences for the calcium carbonate, though the variation is higher than that seen for the DOTP.

Table 7 gives the differences between the actual and theoretical values as a percentage. For the DOTP level it can be observed that all the theoretical levels other than the one for Quant. 2 are under 7% from the actual DOTP levels. For calcium carbonate the results are not as successful. For the theoretical values found from FT-IR, other than Quant. 1, which did not contain calcium carbonate all the theoretical values differ more than 10% different. When using Raman spectroscopy there is slightly more success, with all but Quant. 3 being under 15% different. Based on the differences observed in Table 7, there is more success in correctly predicting the levels of calcium carbonate level when there is a higher percentage of calcium carbonate present within the material. This could be a result of linear fits being used on the data and it therefore

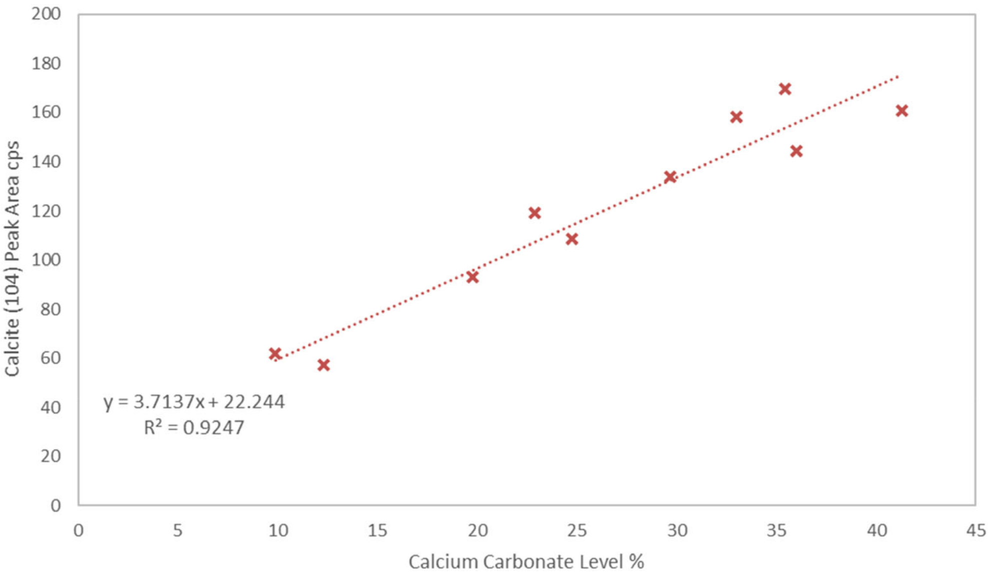

FIGURE 3 Figure showing the calcite (104) peak area against the actual calcium carbonate level in percentage [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 6 Table showing the DOTP and calcium carbonate levels in five additional samples, as well as the peak areas found from both FT-IR and Raman spectroscopy, alongside the theoretical DOTP and calcium carbonate level

Sample ID	DOTP (%)	Calcium carbonate level (%)	FT-IR peak area—DOTP	FTIR peak area—calcium carbonate	Raman peak area—calcium carbonate	Theoretical DOTP level (%)	Theoretical $CaCO_3$—FT-IR (%)	Theoretical $CaCO_3$—Raman (%)
Quant. 1	42.3	0.0	0.212	0.00	0.811	44.6	4.4	−6.4
Quant. 2	16.4	16.4	0.090	0.026	98.9	13.3	19.9	14.0
Quant. 3	44.0	11.0	0.222	0.017	97.7	47.0	16.1	13.8
Quant. 4	12.4	37.1	0.085	0.051	224.3	12.0	31.0	40.1
Quant. 5	33.1	33.1	0.168	0.047	194.2	33.2	29.1	33.9

TABLE 7 Table showing the DOTP and calcium carbonate levels in five additional samples, alongside the theoretical DOTP and calcium carbonate levels calculated in Table 6, with the addition of the percentage differences found in between the actual and theoretical values

Sample ID	DOTP (%)	Calcium carbonate level (%)	Theoretical DOTP level (%)	Theoretical $CaCO_3$—FT-IR (%)	Theoretical $CaCO_3$—Raman (%)	Percentage difference DOTP level (%)	Percentage difference $CaCO_3$—FT-IR (%)	Percentage difference $CaCO_3$—Raman (%)
Quant. 1	42.3	0.0	44.6	4.4	−6.4	5.45	4.35	−6.37
Quant. 2	16.4	16.4	13.3	19.9	14.0	−18.95	20.92	−14.51
Quant. 3	44.0	11.0	47.0	16.1	13.8	6.82	46.25	25.43
Quant. 4	12.4	37.1	12.0	31.0	40.1	−2.91	−16.28	8.21
Quant. 5	33.1	33.1	33.2	29.1	33.9	0.27	−11.97	2.34

Abbreviations: DOTP, dioctyl terephthalate; FT-IR, Fourier transform-infrared.

may be that the use of polynomial fits in the future would resolve some of the discrepancies found here.

The theoretical raw material levels were plotted against the actual raw material levels as seen in Figure 4. Overall, the high R^2 values indicate there is a strong correlation between the actual raw material levels and the theoretical raw material levels. The gradients from the fitted lines demonstrate what was previously seen with the percentage differences, with the DOTP gradient being the closest to 1, suggesting that the theoretical

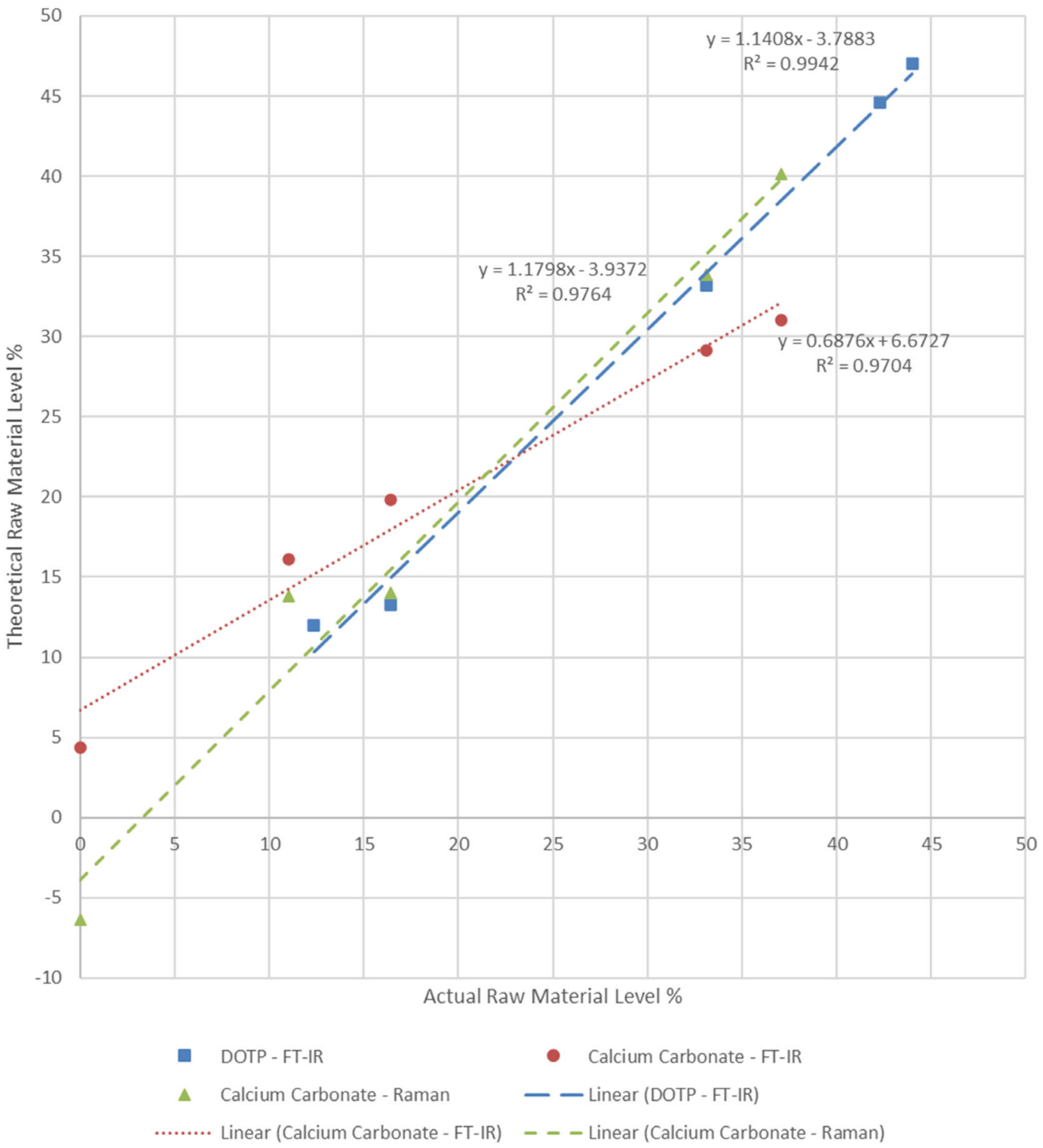

FIGURE 4 Figure showing the actual raw material levels (dioctyl terephthalate; DOTP and calcium carbonate) versus the theoretical raw material levels (DOTP and calcium carbonate) [Color figure can be viewed at wileyonlinelibrary.com]

values found for DOTP are the closest to the actual values for DOTP. The gradient for the calcium carbonate values found through FT-IR are the further from 1 suggesting that this is the least accurate of the predictions made, reflecting what was seen with the percentage differences. The high R^2 squared value found means that these lines could be used to provide an adjustment factor, along with further work, in order to produce a more accurate prediction.

Overall, the results found show that both spectroscopies can be used to estimate the raw materials levels in PVC compound, in an industrial setting. However, further work will be required in order to refine this technique so that it could replace physical testing currently used within the PVC industry.

4 | CONCLUSIONS

The work reported here has demonstrated that:

a. Both FT-IR and Raman spectroscopies can be used to detect, and quantify, DOTP and calcium carbonate filler levels in pPVC.
b. Whilst PHR is used within the PVC industry, the results gave stronger correlations once they had been normalized from PHR to percentage. In all cases the PVC resin and stabilizer levels will need to be estimated.
c. Whilst both spectroscopic techniques gave information that allows the raw material levels to be predicted within a PVC compound, FT-IR spectroscopy is the technique most likely to be utilized.

d. FT-IR spectroscopy gave the stronger correlations, without major discrepancies being caused by the other raw materials present, than observed in Raman measurements.
e. FT-IR spectroscopy also have the advantage of being more widely available, cheaper, and easier to use, except if handheld instruments are considered and can achieve a similar level of results.

Whilst useful information has been observed within the study, further work is still required. There is a need to consider the stabilizer pack level and how this may or may not be influencing the plasticizer and filler responses on the analytical measurement techniques used. There is also a need to investigate other plasticisers and fillers to ensure that a distinction can be made between them, if required. It is only with this additional information that a method can be developed to use spectroscopic techniques to quantify the raw material levels within PVC compound.

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AUTHOR CONTRIBUTIONS

Johannes H. Potgieter: Supervision (equal); writing – review and editing (equal). **Christopher Liauw:** Supervision (supporting); writing – review and editing (supporting). **Robert Sparkes:** Supervision (supporting); writing – review and editing (supporting). **Sanja Potgieter-Vermaak:** Supervision (lead); writing – review and editing (equal).

DATA AVAILABILITY STATEMENT

Data available on request due to privacy/ethical restrictions.

ORCID

Kate S. Irvin https://orcid.org/0000-0001-9661-643X

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