

The Creation of a Novel Predictive Model for pPVC using Spectroscopic Techniques.

K S IRVIN

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The Creation of a Novel Predictive Model for pPVC using Spectroscopic Techniques.

KATE SARAH IRVIN

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Abstract

POLEMERS (Property and fOrmulation predictivE Model for the polymEr industRy using Spectroscopy), a novel model to predict the bill of materials (BOM) and/or the properties of general-purpose plasticised PVC compounds was created for the first time. The polymer industry, as many others, are change adverse, in lieu of the fact that current standard procedures work. However, with an increasingly competitive market, improvements in industrial processes are vital for sustainability. The current process to either develop a new PVC compound fit for purpose or test a competitor's product is extremely time consuming and labour intensive. Many of the tests to be performed are based on technical expertise and experience, which both create potential bias as well as limit the human resources that can be used for it. To that end, this study investigated and created a fast, simple, inexpensive, and fit for purpose method by which BOMs and material properties can be predicted and achieved.

The research conducted herein entails producing a large set of samples of known composition, which were extensively characterised by various chemical measurements as well as physical/mechanical property tests to produce a comprehensive dataset that could be employed for the development of the proposed model. This approach enables the model to make predictions with a high degree of accuracy while minimising the need for extensive and resource-intensive experimental testing.

Key findings indicate that POLEMERS successfully predicts multiple raw material levels and material properties of pPVC for general-purpose applications with industrially acceptable accuracy. FT-IR spectroscopy was found to outperform Raman spectroscopy in predicting raw material concentrations, offering a faster, more accurate, and cost-effective technique that requires less skilled labour. The extensive databank created serves not only as a

foundation for POLEMERS but also as a valuable resource for the industry, offering deeper insights into material properties and guiding future formulation strategies.

POLEMERS has the potential to reduce laboratory staffing costs by nearly 50%, freeing significant time for technical staff to focus on more complex projects. However, the model's effectiveness is currently more pronounced in midrange raw material concentrations, requiring further refinement for higher and lower concentrations and specialised raw materials. Despite these limitations, the initial results are promising, and ongoing refinement and validation are expected to enhance its robustness and applicability.

By introducing this novel predictive model, the industry can benefit from streamlined processes that enhance efficiency and productivity. The ability to swiftly determine the BOMs and material properties of PVC compounds has the potential to revolutionise product development and quality control. Manufacturers can now save valuable time and resources by utilising this cost-effective solution, leading to improved competitiveness and a more sustainable future. This proposed model, while being a first attempt, can clearly be further optimised in future, with a more diverse dataset of compositions and properties.

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Abbreviations and Definitions

ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance
BOM	Bill of Materials
BSI	British Standards Institution
BSS	British Standard Softness
DBM	Dibenzoyl methane
DEHP/DOP	Di(2-ethylhexyl) phthalate/Di octyl phthalate
DINP	Diisononyl phthalate
DOA	Diocetyl adipate
DOTP	Diocetyl terephthalate
DPHP	Dipropyl heptyl phthalate
DSC	Differential Scanning Calorimetry
ESBO	Epoxidized Soybean Oil
FT-IR	Fourier Transform Infrared
GCC	Ground Calcium Carbonate
GP	General Purpose
GP-SEC	Gel Permeation – Size Exclusion Chromatography
ISO	International Organization for Standardization
LDH	Layered Double Hydroxide

NMR	Nuclear Magnetic Resonance
PCC	Precipitated Calcium Carbonate
PHR	Per Hundred Resin
POLEMERS	Property and fOrmulation predictive Model for the polymEr industRy using Spectroscopy
pPVC	Plasticised poly (vinyl chloride)
PVC	poly (vinyl chloride)
QC	Quality Control
RMS	Root Mean Squared
RPM	Revolutions per minute
SBM	Stearoyl Benzoyl Methane
TGA	Thermogravimetric Analysis
THEIC	1,3,5-Tris(2-hydroxyethyl) cyanuric acid
THF	Tetrahydrofuran
uPVC	Unplasticised poly (vinyl chloride)
UV	Ultraviolet

1. Introduction

1.1 Background to the Investigation

Poly (vinyl chloride) compound has been commercially available for one hundred years. During this time, the technology for both the production and processing has changed dramatically (Braun, 2001). Many of the changes in raw materials, especially in recent years, are the direct result of legislative changes dictating which additives can be used within compound PVC (Al Salloum et al., 2015; Turner, 2016). It is because of these many advancements that there is a need to constantly assess the PVC technology used and ensure that stringent test methods are available which allow fast and accurate testing of the many properties of compound PVC (Mehta et al., 2014; Quennehen et al., 2015).

There are two main types of PVC compound, unplasticised or rigid PVC and plasticised or flexible PVC. The type of PVC compound used is dependent on the final use of the material. Different raw materials will be used depending on the desired properties. As there can be huge variations in the properties of a PVC compound, a large variety of product testing is completed in the PVC industry. This testing occurs in the formulation stage, the production stage and even at the end of life. At the formulation stage, the material is developed to meet customers' specifications or to match existing samples. This process can include many tests to ensure that the material developed meets all the parameters required. During the production of PVC compound, quality control testing plays a vital role (Cao et al., 2016) and is completed at each step, from the raw materials through to the final product. Whilst important, the tests completed during QC testing are normally fast and simple and not as extensive as during the formulation stage of PVC production.

1.1.1 Industrial Testing

At both the formulation and QC stages, most of the testing is mechanical testing, such as hardness testing and tensile testing, or basic thermal testing, such as Congo Red heat stability. When formulating new grades of PVC all new materials will have their heat stability and relative density tested, and then the further testing completed will be determined by the PVC type. When testing uPVC, Vicat softening point and impact testing are also frequently tested. When testing pPVC the hardness of the material will be tested, normally alongside its tensile properties. Once a developed material meets the specification with these basic tests, then further application-specific testing will be completed. It is a combination of these core tests along with the application-specific tests that determine whether a material is suitable for the intended application.

1.1.2 Standardised Testing Procedures

Of the tests completed within the PVC industry many of them are outlined by standards from BSI, ISO, or ASTM (Wypych, 2008). The test methods specify the procedures to complete the test, including sample dimensions, test conditions and conditioning times. Conditioning times for most tests range from 24 hours to 168 hours before they can be tested. This conditioning period, whilst important, creates the issue that if a new grade is developed, certain properties, such as British Standard Softness cannot be obtained for seven days. If any further changes are required a further seven days of conditioning will be needed extending the development time significantly. This seven-day conditioning period also creates an issue when completing QC testing, in a commercial, production environment. This has resulted in alternative methods, such as testing at 24 hours instead. Whilst this can provide a quicker test, it runs the risk of higher variation in the results and therefore issues not being realised until the material is already with the customer.

1.1.3 PVC Formulations

To successfully develop new grades of PVC compound, a comprehensive understanding of various factors is essential. Not only when considering the test methods employed but also all the variables that come into play, spanning from the selection of raw materials to the ultimate properties of the final product.

However, the current testing procedures employed within the PVC industry tend to be time-consuming and resource intensive. As a result, the development and release of new materials to customers face significant delays. This prolonged process creates long lead times, which can be detrimental to both the company and its clients.

To address this issue, it is imperative to find a solution that enables the testing of PVC samples to be completed within hours rather than weeks. By streamlining and expediting the testing phase, manufacturers can significantly reduce the overall development timeline. This not only increases efficiency but also allows for a faster response to customer demands and market trends.

The implementation of a streamlined and accelerated testing process within the PVC industry is crucial for expediting material development, reducing lead times, and meeting the demands of a rapidly evolving market.

1.1.4 A Spectroscopic Solution

Within the literature, whilst physical testing is completed, much of the testing completed relies upon analytical testing of the material. One of the most common methods of testing used is FT-IR spectroscopy and Raman spectroscopy (Gilbert et al., 2013; de Souza et al., 2009; Wang et al., 2015).

These spectroscopic techniques have been used to consider PVC resin, plasticiser, filler, and the stabiliser packages in use. This shows that the techniques have the capability to test various aspects of compound PVC. Within industry FT-IR spectroscopy and other

techniques are already utilised for individual components, and so further developing the use of such instruments within the industry is not completely out of the question. For FT-IR and Raman spectroscopy to add true value to the PVC formulations process, they would need to be used quantitatively alongside existing techniques.

1.1.5 Spectroscopic Techniques in the PVC Industry

Over the last decade many industries started to utilise spectroscopic based predictive models to streamline industrial processes (Le et al., 2012; Song et al., 2016). This is something that could be transferred to the PVC industry. If the numerical data obtained from a Raman or FT-IR spectrometer were incorporated in a model, there is every possibility that this could revolutionise both the development of new PVC grades but also the QC processes in use. Testing for PVC developments which used to take over a week could potentially be reduced to half a day. From a business standpoint alone, this would be extremely beneficial as it would also result in reduced batch cycle times and holding periods within production. The creation of the model itself is not the only advantage. To create a model, a completed characterisation of varying PVC formulations would need to be carried out. This analysis could lead to finding relationships, which have not been previously observed within the literature, as most research into PVC often does not complete the full characterisation of the material.

1.2 Aim of the Investigation

The aim of the investigations was to create a comprehensive databank of different pPVC formulations to feed into the model and thereby determine relationships between raw material quantities, properties, and spectroscopic intensities. Therefore, allowing the creation of a predictive model, allowing pPVC formulations to be predicted from spectroscopic data and the materials properties to be predicted from the formulation.

1.3 Objectives

1. Determine the properties to be evaluated alongside suitable spectroscopic techniques, based on industrial standards.
2. Identify the raw materials having the biggest impact on the materials properties.
3. Create 96 different PVC formulations based on the raw materials identified in and complete testing on these to create a databank for interrogation.
4. Create a predictive model using the data acquired, using statistical relevance to inform formulations from the spectroscopic results, and the properties from the formulation.
5. Test the model on for accuracy, repeatability, and applicability in industry, using a test dataset.

1.4 Scope of the Investigation

The scope of the investigation is limited to plasticised PVC compound, with plasticiser and filler addition between 0 PHR and 100 PHR. The physical testing will be limited to softness testing, stability testing, density testing and tensile testing, alongside spectroscopic testing.

1.5 Hypothesis

Accurately deconvoluted trained vibrational spectroscopic data can predict pPVC properties and/or the BOM in a quick and efficient way, using the model (**Property and fOrmulation predictive Model for the polymEr industRy using Spectroscopy = POLEMERS**).

1.6 Lay-out of the Thesis

The thesis is organised in the following manner:

Chapter 1 – Introduction

Chapter 2 – Theoretical Background – Background to PVC compound, the industry, and the need for investigation – Objectives 1 and 2.

Chapter 3 – Literature Review – Exploration of the technologies and tests used within the industry and academia – Objectives 1 and 2.

Chapter 4 – Methodology – Outline of the preparation and testing procedures used – Objective 3.

Chapter 5 – Spectral Analysis – Investigation into the most effective system to interpret the spectral data collected – Objectives 3 and 4.

Chapter 6 – Phase 1 -3 Results and Discussion – Overview of the results found for phase 1 -3 of work completed, forming the backbone of the predictive model - Objectives 3 and 4.

Chapter 7 – Predictive Model and Phase 4 – Overview of the creation and functionality of the predictive model and the testing of the model further dataset - Objectives 4 and 5.

Chapter 8 – Financial Implications – Overview of the financial implications of such a model on the PVC industry

Chapter 9 – Conclusions – Final conclusions on the investigation and any further work that could be completed.

2. Theoretical Background

The purpose of this chapter is to provide the reader with the necessary background/theory to underpin the data obtained and the experimental interpretations made.

A myriad of polymer compounds are produced annually. Worldwide production was 367 Mt in 2020 (Plastics Europe, 2021) and global distribution is dominated by Asia (50%) (Figure 2-1 (a)) Packaging makes up 41% of usage in Europe (Figure 2-1 (b)). Although PVC was discovered in 1835, it was only after the discovery of plasticisers in 1926 that the brittleness of PVC could be eliminated, producing a product that is flexible. PVC has become one of the most versatile polymers in commercial applications due to plasticisers (European Union, 2022). It is therefore not surprising that it holds 10% of European market share, resulting in the third highest market share, in Europe (Figure 2-1 (c)).

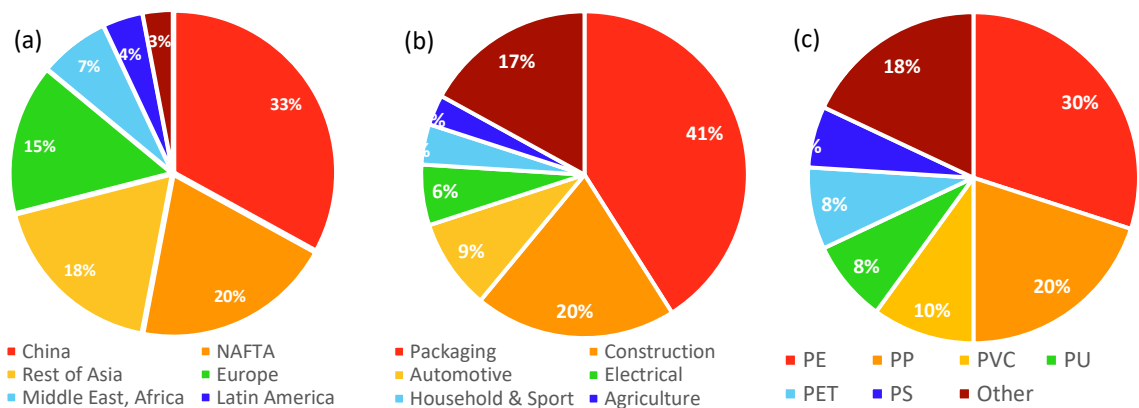


Figure 2-1: (a) Global plastic production (2020); (b) European plastic demand by market segment; (c) European plastic.

2.1 PVC Compound

PVC compound can be categorised as a thermoplastic polymer that becomes softened when heated and hardens upon cooling (Biron, 2016). Compound PVC can be split into two types: unplasticised or rigid PVC, and plasticised or flexible PVC. It has the advantage that it is extremely cost effective, and this, along with its versatility, gives it an edge over many other polymers (Alsabri and Al-Ghamdi, 2020).

Rigid PVC is compound PVC that has little to no plasticiser in it and an average glass transition temperature of 87°C. UPVC has limited malleability at room temperature.

Despite this, it is used for numerous applications, many of which fall into the building and construction sector (Amorim et al., 2022). The main applications for uPVC are window frames, pipes, and electrical conduits. However, it can also be used for bottles and packaging, normally in a transparent or translucent form (Barnard et al., 2020; Coaker and Fire Retardant Chem, 1996; Schyns and Shaver, 2021).

Flexible PVC is PVC compound that contains plasticiser, which results in a lower glass transition temperature and therefore creates a more malleable material (Yang et al., 2015). PPVC can be created across a vast softness range, meaning that it is an extremely versatile material. In many cases it has been used as a replacement for rubber (Titow, 1984). It is commonly used for wires, cables, medical tubing, footwear, and window gaskets, as well as some packaging material (Al Salloum et al., 2016; Biedermann and Grob, 2006; Grisa et al., 2011; Kumar, 2019).

In the current global plastic waste crisis, with microplastics being found throughout the oceans and planet, a big positive of PVC is that it can be recycled with relative ease (R. Kumar et al., 2021). However, it is important to first determine the type of PVC (rigid/flexible) to ensure that the PVC can be successfully recycled due to many post-consumer PVC products containing substances that are now banned under various legislation or in various applications (European and Directorate-General for, 2022)).

2.2 BOM Design

The overall process of developing a new BOM of compound PVC can be seen in Figure 2.2.

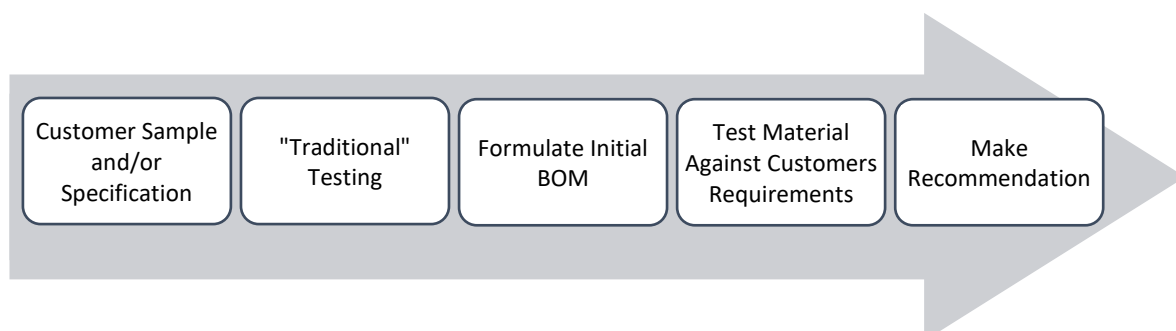


Figure 2-2: Flowchart showing the creation of new materials for customers within the PVC industry.

The first step is that the customer will provide either a specification and/or a sample of the material they want. If the customer provides a sample, then the second step will be to test this sample to determine the properties, and therefore establish which of these are the key properties required by the customer. Once the required properties have been established, either through a supplied specification, or testing, the fourth step is to create a potential BOM (Wickson and Grossman, 2008). This BOM is normally formulated through estimations and educated guesses based on previous work. Once an initial BOM is established, it will be produced and will then undergo testing. If the material matches the requirements established in steps one and two, a recommendation will be made, and a sample will be produced for the customer to trial in their production process. If the properties do not match, then the formulation will be adjusted and retested until a suitable formulation is found. For a flexible PVC material, each round of testing takes at least 7 days. This means that the process can be long and intensive. Additionally, experience is required to create a formulation that will meet the required specification, therefore the more experienced the “user” is, the faster the process will be. As with most commercial processes the faster something can be completed the more cost effective it is.

2.3 PVC Composition

Unlike many other polymers PVC compounds are complex with several different additives being required to create a product that can be sold on commercially.

2.3.1 PHR – Per Hundred Resin

Formulations across the PVC industry are expressed using a “unified system” where all raw materials are expressed as a ratio, so that the PVC resin content is 100. This ratio is therefore called “parts per hundred resin” or more commonly PHR. PHR offers a reliable and uniform method of determining the amount of PVC resin present in a formulation. Different vendors and manufacturers can make sure they are utilising the same amount of

PVC resin by describing it in terms of PHR, even if they use various scales or measurement techniques. This makes it easier to standardise the formulation and guarantees that the end product's quality and characteristics are constant. Additionally, PHR makes it simple to compare various formulations and aids in both the creation of new formulations and the optimisation of existing ones. To demonstrate this,

Table 2-2 shows three formulations in both percentage and PHR. As can be seen across all three BOMs, when using percentage each raw material is present in a different quantity, whereas when using PHR the raw material addition rates are all displayed relative to PVC which is fixed at 100, therefore making comparisons between the materials far simpler.

Table 2-1: Table showing three different PVC BOMs in both percentage and PHR.

Raw Material	BOM 1 (%)	BOM 1 (PHR)	BOM 2 (%)	BOM 2 (PHR)	BOM 3 (%)	BOM 3 (PHR)
PVC Resin	61.73	100.00	58.14	100.00	54.95	100.00
Plasticiser	24.69	40.00	29.07	50.00	32.97	60.00
Filler	12.35	20.00	11.63	20.00	10.99	20.00
Stabiliser	1.23	2.00	1.16	2.00	1.10	2.00

2.3.1.1 Raw Materials

PVC resin the raw PVC polymer, is brittle, unstable, and unusable on its own. To render PVC useful and fit for purpose/application, several additives can be used. These can be split into five defined categories: PVC Resin, Stabilisers, Plasticisers, Fillers, and Specialty Additives (Zweifel and Amos, 2001). Each of these raw materials plays a key role within PVC compound, whether it is to offer specific properties for both processing and/or the product, or to provide cost savings (Sánchez-Domínguez and Rodríguez-Abreu, 2016; Schiller, 2015).

2.3.2 PVC Resin

PVC is a synthetic polymer with starting materials ethylene and chlorine. The ethylene used for PVC resin is normally derived from the cracking of either oil or natural gas hydrocarbons, after which it is separated from any co-products (Baitz et al., 2015). The chlorine used in

PVC resin is manufactured alongside the production of caustic soda and is produced by cell electrolysis of salt water. Around 35% of Europe's chlorine production goes into PVC production (Kumar et al., 2021). Whilst crude oil is used in the production of the PVC, the inclusion of the chlorine means that 57% of the resin is chlorine by weight. This makes it a greener option when compared to other traditional polymers that are almost 100% crude oil based (Correa et al., 2019).

Figure 2-3 shows the overall process from natural gas/oil and salt water (brine) through to compound PVC. The oxychlorination of ethylene and chlorine produces ethylene dichloride.

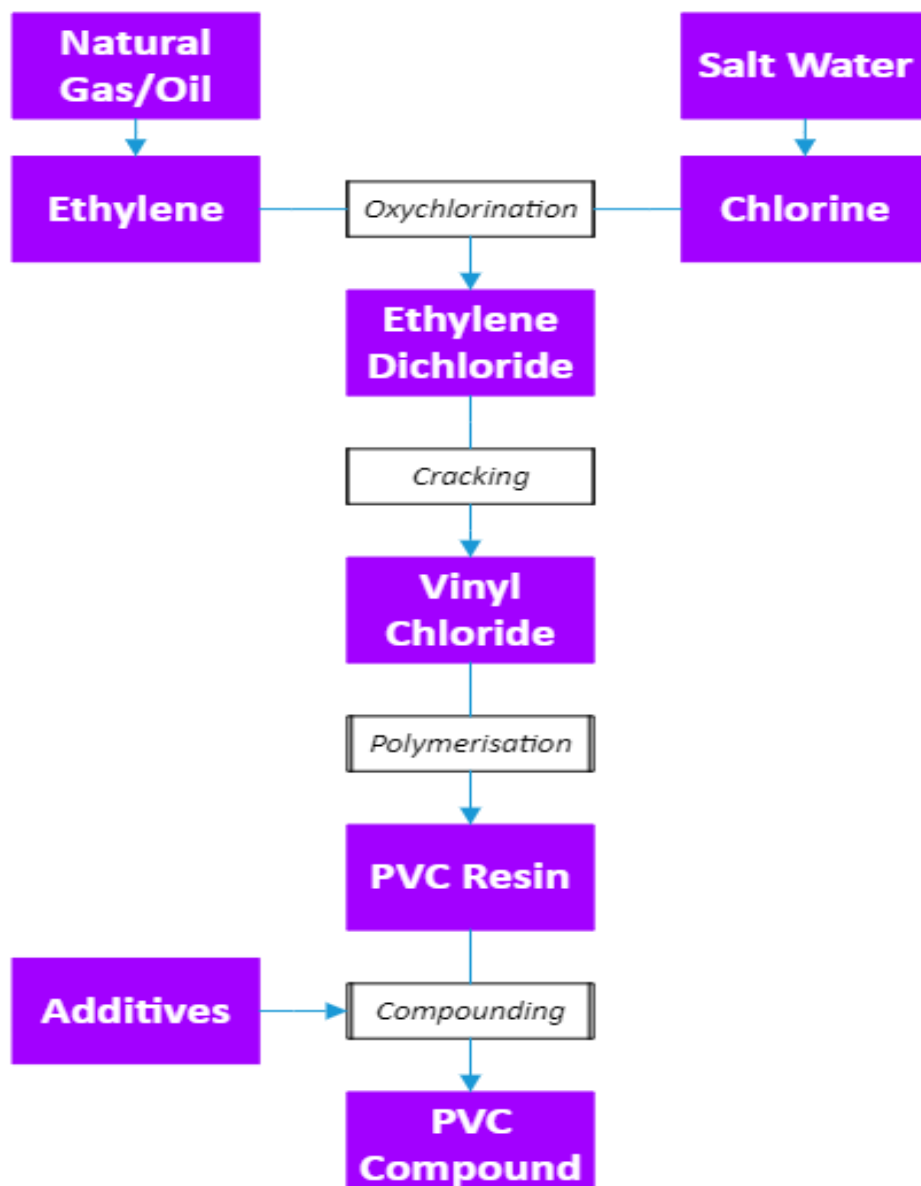


Figure 2-3: Flow chart showing the production process for PVC compound from Natural Gas/Oil and Salt Water (brine).

This is followed by cracking to produce vinyl chloride monomers, which are polymerised into PVC, as shown in Figure 2.6, before being compound with other raw materials to compound PVC (Nuraini, 2020).

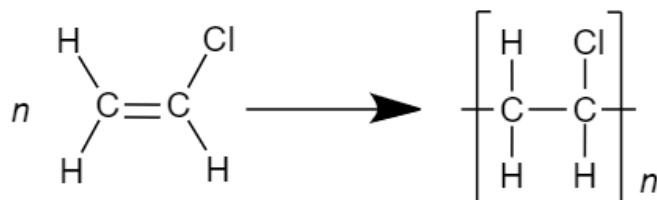


Figure 2-4: Polymerisation of vinyl chloride monomers to PVC.

There are three different processes used on a commercial scale to produce PVC resin. These are suspension, emulsion, and bulk polymerisation. Whilst resin produced from emulsion and bulk polymerisation are used for making speciality compound PVC, 80% of resin produced is suspension resin (Guo et al., 2017).

2.3.2.1.1 Suspension Resin

To produce suspension, resin raw materials (vinyl chloride monomer, suspending agents, and water) are all agitated at high speed within a reactor. This process forms droplets of the vinyl chloride monomer. An initiator is added to kickstart the polymerisation of these vinyl chloride droplets into PVC suspension resin. This process is completed under controlled temperatures and pressure to create a slurry. This slurry is stripped of any unreacted vinyl chloride monomer and the excess water is removed. The remaining solid is dried to form the final product, at which point it is tested in line with the specification for that resin (Patrick, 2005; Wheeler, 1981).

PVC resin is produced with various polymer chain lengths and therefore various molecular weights and viscosities, resulting in different properties (Nass and Heiberger, 1986). Within the PVC industry the different grades of PVC are referred to by a K value.

Table 2-2 provides an overview of some of the common K values used for flexible PVC. Due to the nature of the method in which the PVC resin is produced, the exact length of each

polymer chain will vary both between the batches, as well as within the same batch. For example, whilst a grade may be labelled as K70, it will in fact be $K70 \pm 2$.

For pPVC the most used resin is K70 suspension resin. This is inexpensive and readily available, as well as being easy to process and the most versatile. As can be seen in Table 2-2, a decrease in the K value result in higher flow and higher gloss. Lower K value PVC would normally be used for moulding applications, due to these properties. An increase in the K value results in higher resilience in the product and gives a more matte or even a textured finish (Kroushl, 2008).

Table 2-2: Table showing a range of PVC resins with difference K values used for PVC compound, giving their purpose, degree of polymerisation and relative cost.

K-Value	Purpose	Degree Of Polymerisation	Cost
60	Very high gloss, very high flow.	800 +/- 50	£
66	High gloss, high flow.	1000 +/- 50	£
70	Standard GP resin. Used for pPVC.	1200 +/- 50	£
80	Low gloss, high heat resistance.	1800 +/- 100	££
90	Very low gloss, very high heat resistance.	2400 +/- 100	£££
100	Very low gloss, very high heat resistance.	3000 +/- 100	££££

It is impossible on a commercial scale to achieve a perfect product, regardless of the way in which PVC is produced. Within the PVC chain there will always be irregularities that cause degradation of the material. Two common irregularities are shown below Figure 2-5. Both irregularities create labile chlorine, which then promotes destabilisation of the chain (Rogestedt and Hjertberg, 1992). It is for this reason that stabilisers must be used.

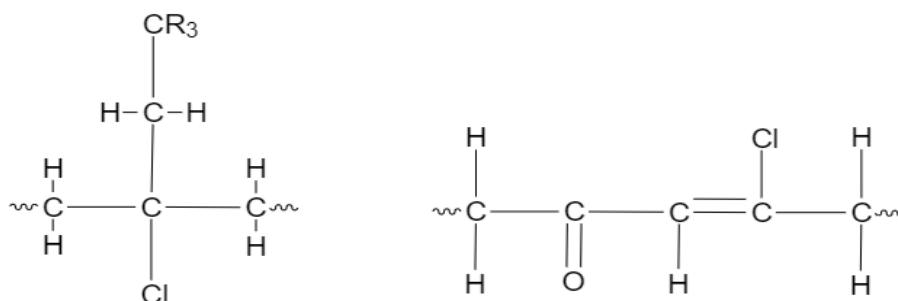


Figure 2-5: Left - Tertiary chlorine structural irregularity. Right – Keto allylic structures generated by thermos-oxidative processes.

For this work K70 will be used as the base resin, additional K value resins will also be investigated.

2.3.3 Stabiliser Packages

Whilst all PVC compounds require stabilisation to enable processing and the production of usable products, these stabilisers are rarely used in isolation. Therefore, other raw materials are used that make up a stabiliser package (Schiller, 2021). Calcium and zinc stabiliser systems will normally consist of, primary stabilisers, secondary stabilisers, co-stabilisers, antioxidants, lubricants and process aids

Depending on the requirements and/or application of the PVC product, a combination of all, or some of these will be used to achieve the desired effect. application.

Table 2-3 gives some applications, stabiliser loadings and common points that would need to be considered. As shown in the table, the loadings can change significantly based upon the application, with pPVC having a range from 0.5 – 12 PHR dependant on application.

Table 2-3: Tables showing some common applications of both pPVC and uPVC, along with typical stabiliser loadings, in PHR and some additional notes regarding the raw materials and/or properties required for these applications.

Application	Typical Stabiliser Package Loading (PHR)	Additional Notes
PPVC – GP Extrusion	1 – 4	Standard for pPVC GP extrusion.
PPVC – GP Moulding	2 – 6	Addition of co-stabilisers.
PPVC – Cables	4 – 12	Higher in secondary stabiliser, such as hydrotalcites.
PPVC – Medical Tubing	0.5 – 2	Limited raw materials used to maintain clarity.
UPVC – GP Extrusion	3 – 5	Standard for uPVC GP extrusion.
UPVC – GP Moulding	4 – 6	Requires higher stability, colour retention and higher gelation.
UPVC – Windows	4 – 6	High brightness and colour stability.
UPVC – Pipe	2 – 4	High external lubrication.

2.3.3.1 Primary Stabilisers

Primary stabilisers are one of the most important additives in PVC compound. Stabilisers limit the degradation of the PVC resin to allow the resin to be processed and to increase the material's lifespan (Biron, 2020). There are three types of PVC degradation: oxidative, UV and thermal degradation. Depending on the application of the PVC product, the stabiliser package may need to protect it from all three modes of degradation.

Degradation starts at either the chain ends or at chain irregularities created during resin production (Wypych, 2020). These regions have weakly bonded, labile chlorine atoms that are more readily lost. Figure 2-6 shows the typical process of degradation within PVC resin.

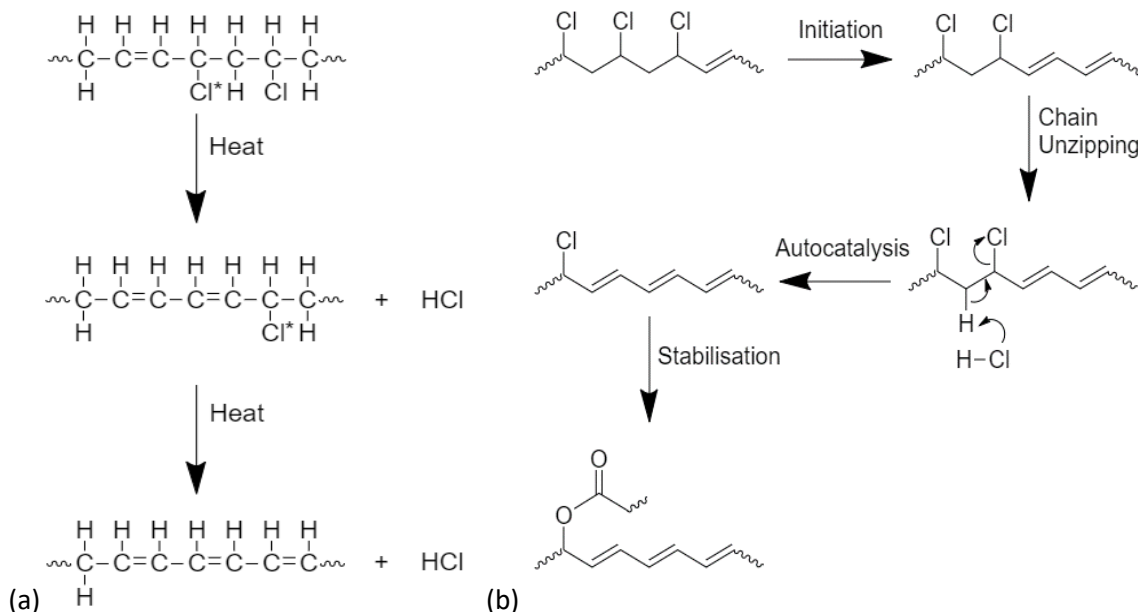


Figure 2-6: Figure showing (a) the release of hydrochloric acid from the PVC chain and (b) showing each step of the degradation of PVC including how hydrochloric acid catalyses degradation and stabilisation.

The degradation of PVC starts with the loss of a labile chlorine which abstracts a hydrogen producing hydrochloric acid. Since hydrochloric acid is a strong Lewis acid, it can catalyse the dehydrochlorination of the PVC backbone, it is important to limit this as much as possible. The dehydrochlorination results in the creation of conjugated polyenes that destabilised the system and result in further degradation, and an unusable material. This increased conjugation changes the polymer system's colour and the material properties (Pickett, 2018). This degradation, and its ability to destabilise the entire polymer chain, is the reason that stabilisers are required within the compound PVC (Holsopple, 1993).

Thermal stabilisers will have one or more of the following features to limit degradation:

1. Act to replace/displace the active, labile groups such as the allylic/tertiary chlorine.
2. Act to make pro-degradation molecules inactive.
3. Interrupt and inhibit the chain conjugation and the elimination of hydrochloric acid.

Most stabilisers also act to limit the auto-catalysation by capturing and/or neutralising the hydrochloric acid being released (Folarin and Sadiku, 2011).

2.3.3.1.1 Lead Stabilisers

For many years, the most used stabilisers in the UK and Europe were lead based stabilisers, the use of which was banned in 2015 due to the various health concerns associated with the use of lead containing products. Lead-based stabiliser systems are still used in some parts of the world due to the attractive cost basis and excellent stabilising performance (Asawakosinchai et al., 2017; Wallenwein, 2006; Zhang et al., 2020). Lead soaps are normally a combination of lead soaps and lead salts (Schiller, 2021), including, lead stearate, dibasic lead stearate, dibasic lead phosphite and tribasic lead sulphate.

Basic lead compounds are excellent hydrochloric acid scavengers and bind hydrogen chloride during the decomposition of PVC. The resulting lead chloride is very stable, insoluble in water and does not encourage the decomposition of PVC. Lead stabilisers are also excellent light stabilisers (Chabira and Mohamed, 2012).

2.3.3.1.2 Tin Stabilisers

For some applications other stabilisers are needed, especially when high clarity is required, tin-based stabilisers are often used for this purpose. These are liquid stabilisers which give high clarity and excellent stabilisation to compound PVC. However, tin stabilisers are expensive to use and are reserved for specific applications, such as high clarity or outdoor applications due to their UV stabilising properties (Song et al., 2022; Wypych, 2008). PVC tin stabilisers are based on methyl, butyl or octyl ester groups (Arkiş, 2008) and can be categorised into thio acid monoesters, mercaptides and dicarboxylic monoesters and result in greater UV stability when compared with other stabilisers, as well as providing first-rate colour-hold in materials.

2.3.3.1.3 Calcium Zinc Stabiliser

The urgent need for stabilising additives which were cheaper and less toxic drove the investigation into combinations of metal soaps such as calcium, magnesium, zinc, barium, etc. (e.g., stearates and laurates) (Ambrogi et al., 2017). As such, a combination of calcium stearate and zinc stearate in varying ratios is now used (Zhang et al., 2020).

Metal stearates can displace labile chlorines at defect sites on the PVC backbone. This is an incredibly valuable function, it prevents the initial dehydrochlorination, limiting the production of hydrochloric acid and the conjugation of the polymer chain. Metal stearates react with hydrochloric acid to form metal chlorides and stearic acid. However, they fall short when compared to the hydrochloric acid reaction capacity of lead-based stabilisers, and so need to be used at higher addition rates (Atakul et al., 2005; Ye et al., 2019). A drawback of the use of zinc stearate is the zinc chloride salt, produced from the reaction between zinc stearate and hydrochloric acid. Zinc chloride salt is a strong Lewis acid which can catalyse the degradation of PVC by reacting with a labile chlorine and initiating the conjugation of the polymer chain. This leads to what is known as “zinc burning” where the rate of degradation is much quicker than formulations containing less zinc (Wu et al., 2018). There are two ways to circumvent this problem: the first is to use zinc stearate in conjunction with calcium stearate. In the presence of calcium stearate, zinc chloride undergoes an ester exchange reaction producing zinc stearate, which can then be used to stabilise the material and calcium chloride, which does not catalyse PVC degradation, since it is a weak Lewis acid. To utilise this, a ratio of 60:40 calcium stearate and zinc stearate has been shown to give a synergistic effect (Maou et al., 2022). The second option is to use a co-stabiliser that can form complexes with zinc chloride, which prevents the autocatalytic behaviour, such as beta diketones (Li et al., 2013).

2.3.3.1.4 Other Stabiliser Systems

Whilst calcium and zinc stearate stabiliser systems perform well in many applications, there are still some applications in which other options are considered. For applications where a highly transparent material or high gloss flexible moulding is required, barium/zinc based stabiliser can be used (Burley, 1997). There is also a general trend towards the use of “organic based stabilisers”, considered better for the environment, due to limiting the use of “heavy” metals. However, these systems are far more expensive (Asawakosinchai et al., 2015; Jubsilp et al., 2022). For this work a calcium stearate and zinc stearate stabiliser system will be used as is common for GP PVC.

2.3.3.2 Secondary Stabilisers

Secondary stabilisers are used in conjunction with primary stabilisers to further enhance the stabilising effect of the stabiliser package. They mostly consist of acid scavengers, with common secondary stabilisers including hydrotalcites, magnesium hydroxide, zeolites, epoxidized soya bean oil and calcium hydroxide (Benaniba et al., 2003; Folarin and Sadiku, 2011). In this work a hydrotalcite type 1 will be used to give added stability to the material.

2.3.3.3 Co-Stabilisers

Co-stabilisers are used to give final adjustments to a material, such as giving colour hold or brightening effects. They can remove labile chlorines to prevent degradation and unzipping, react with hydrochloric acid, as well as being able to form complexes with zinc salts, which can help prevent zinc burning. Unlike secondary stabilisers, co-stabilisers have negligible effect without primary stabilisers, and are used in low loadings. Examples include THEIC, DBM, SBM and pentaerythritol. Co-stabilisers are more commonly used in uPVC, as more robust stabilisation is required (Benavides et al., 1996; Wang et al., 2006).

2.3.3.4 Antioxidants

Antioxidants play an integral part in the stabiliser pack, as they are used to limit oxidative degradation. The oxidation of PVC can function as an initiator for further degradation. Oxidation often occurs at structural defects from PVC resin production. Antioxidants act to stop this by terminating the radical produced during oxidation (Cortolano, 1993). The most used antioxidants used in PVC are phenolic based antioxidants, though for some applications, other options must be considered (Wegmann et al., 2002). In this work antioxidant 76 will be used in line with the industry standard.

2.3.3.5 Lubricants

Lubricants are used in PVC compound to reduce the friction generated during processing to prevent degradation. Lubricants can be divided into two types: internal lubricants and external lubricants. Both types of lubricant reduce the heat generated during processing and therefore the degradation of the material. External lubricants reduce the friction between the PVC and the processing equipment, while internal lubricants are used to reduce the friction between the polymer chains. A mixture of internal and external lubrication is used and the ratios of each is optimised based on the application. Whilst some lubricants only have one function (internal/external), there are several lubricants that display both internal and external properties (Harper and Petrie, 2003). The more polar a lubricant, the more internal its lubricating action would be, and the more non-polar a lubricant is, the more external its lubricating action will be (Spiekermann, 2008). Whilst most lubricants will hinder the gel time of the material, oxidised lubricants are a specific type of external lubricant that can provide additional metal release and promote gelation. This action means that they can also be used to provide functions like those of process aids (Treffler, 2005). In this work stearic acid will be used in line with the industry standard.

2.3.3.6 Process Aids

Process aids are primarily used to promote fusion and to increase the gelation by increasing the cross linking within the polymer matrix. The increase in gelation leads to an increase in melt strength, which provides an increase in the mechanical properties of the PVC compound, such as impact properties and elasticity (Treffler, 2005). Process aids can also be used to provide an increase in the materials clarity. Many process aids will also provide a lubricating function. It is worth noting that process aids are more often used in uPVC, therefore in this work no process aids will be used.

2.3.3.7 Flexible Stabiliser Packages

Whilst many different raw materials can be included in a stabiliser package, most of these are primarily used in uPVC. PPVC Stabiliser packages remain basic, because the plasticiser lowers the melt viscosity, provides lubrication, and therefore results in less shear limiting the degradation during processing (Niaounakis, 2013; Shrivastava, 2018).

Table 2-4 gives an overview of the general raw materials and the percentage loading used in a general-purpose flexible PVC stabiliser package. This is the basis of flexible PVC stabiliser packages. Tweaks and additions to this base can be used to create a suitable pack for each application (Coffin, 1984). For example, if a high-temperature cable is required, the hydrotalcite will be used at a higher percentage, whereas for a moulding grade, the hydrotalcite would normally be lower with a high addition rate of the other raw materials.

Table 2-4: Table of typical stabiliser package components and composition.

Purpose	Additive	Quantity Used
Primary Stabiliser 1	Calcium Stearate	20 – 60%
Primary Stabiliser 2	Zinc Stearate	20 – 60%
Secondary Stabiliser	Hydrotalcite	20 – 60%
Antioxidant	Phenol Based AO76	1 – 10%
Lubricant	Stearic Acid	1 – 10%

2.3.4 Plasticisers

Plasticisers are materials that can be used to lower the glass transition temperature of plastic to increase the flexibility of the product. As well as making the material flexible, they are used to increase the flow, extension and processability. Whilst plasticisers are used to increase the softness of a material within pPVC, in low concentrations plasticiser can also be found in uPVC for binding, stabilising, and lubricating purposes (Buszard, 1984). Despite having been used in PVC for one hundred years, the mechanism of plasticisers has not yet been fully explained. Two mechanisms were developed in the 1940's: these are the lubricity theory and the gel theory. The lubricity theory suggests that plasticisers act in a comparable way to internal lubricants, allowing movement of the polymer chains over each other. This theory depends on the plasticiser working as both a solvent and a lubricant in segments. The gel theory suggests the existence of solvating dipoles when plasticiser is added to PVC, with areas being solvated and then de-solvated across the polymer chain to increase the motion of the polymer chain (Daniels, 2009; Marcilla and Beltrán 2017). Combining both these theories, the 1940's yielded the free volume theory. This theory suggests that plasticisers work by entering the "free space" between the polymer chains and "pushing" the chains apart. This free space changes with temperature, explaining why a change in the plasticisation occurs when approaching the T_g (Marcilla and Beltrán 2017). Whilst all three of these classic theories explain some aspects of plasticisation, none explain all the aspects. In more recent years, mathematical models have been developed to explain the plasticisation of compound PVC. These are based on the free volume theory, such as the one proposed by Mauritz and Storey (1988) alongside structural factors, such as the number and size of side chains and the overall length of the plasticiser molecules. The plasticisation process decreases the material's glass transition temperature from approximately 80°C to below room temperature. The glass transition temperature is the

point at which a material goes from a “glass-like” rigid solid to a flexible more “rubber-like” compound (Al-Malaika et al., 2017). It is worth noting that different plasticisers have a different level of plasticising compared to their concentration within the PVC compound. This is referred to as the efficiency of a plasticiser. The greater the efficiency, the less plasticiser is required to achieve that level of flexibility.

2.3.4.1 Primary Plasticisers

Since their inception, several different primary plasticisers have been used within pPVC. Many have since been restricted or banned due to environmental and/or health concerns. There are a vast number of plasticisers available on the market. GP plasticisers can be divided into two main groups: phthalate plasticisers (ortho-phthalates) and terephthalate plasticisers. Within the industry, when the term phthalate free is used, this refers specifically to ortho-phthalates. Figure 2-7 shows the difference in structure between an ortho-phthalate and a para-phthalate.

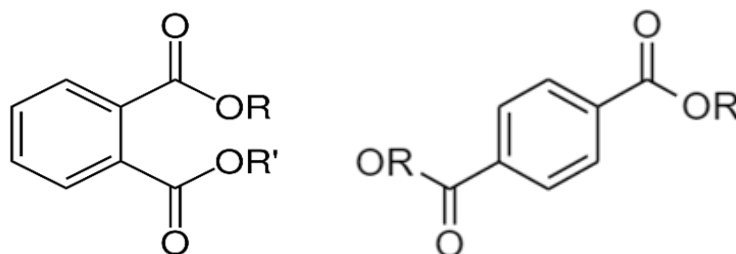


Figure 2-7: Figure showing the structural differences between an ortho-phthalate (left) and a para-phthalate (right).

For many years, DEHP was used in most general-purpose applications, as well as some specialty applications. Its popularity was due to its low cost, high efficiency, and stability within pPVC compound (Ali Zulfikar et al., 2022). However, DEHP is restricted in its use under REACH within the EU and restricted under Proposition 65 in the USA (Reddam and Volz, 2021; Silano et al., 2019). These restrictions were put into place as evidence was found that showed it to be an endocrine disruptor. As a result, the use of DEHP has dropped significantly across the globe, though it is still used in areas where the products are not expected to enter an area in which it is restricted (Salazar-Beltran et al., 2018; Wang

and Qian, 2021). It is also still being permitted in the EU under licence when being used for specific purposes, such as in the production of blood bags (Larsson et al., 2021). Since the removal of DEHP from use (within Europe) the plasticiser market is now divided between several different plasticisers. The most common for GP PVC are DINP and DOTP. They are both slightly less efficient than DEHP, overall providing comparable properties. DINP is also restricted under Proposition 65 in the USA.

Table 2-5: Table giving an overview of some plasticisers commonly used within various pPVC applications. With higher efficiencies being represented by more ●.

Plasticiser	Impact on Formulation	Efficiency
DINP	Phthalate-containing; good compatibility and fusion.	● ● ●
DPHP	Phthalate-containing; high compatibility, with improvements in UL94, heat-aged stability, melt flow index, and tensile strength.	● ●
DOTP	Non-phthalate alternative to DINP; suitable for general non-phthalate PVC grades.	● ●
DOA	Non-phthalate; high melt flow index, good low-temperature flexibility, with considerations for thermal-aged tensile testing, UL94, and extractability.	● ● ● ●
TOTM	Increased stability, heat ageing and tensile properties. As well as a decrease in extractability (increased oil resistance).	● ● ● ●
TML810	Increased stability, heat ageing and tensile properties.	● ● ● ● ●
Ultramol IV	Additional options based on specific requirements.	● ●
ESBO	Non-phthalate: added at low rates to improve thermal stability; careful use due to potential colour impact.	● ● ●

There are a vast range of plasticisers available on the market. Some of these can be used alone or in combination with GP plasticisers to provide additional properties, whilst keeping the raw material costs down (Meyers, 2002).

2.3.4.2 Secondary Plasticisers

The plasticisers discussed so far are used to provide most of the plasticising effects, there are times when a low dose of an additional plasticiser can also be used. These are called secondary plasticisers and differ from primary plasticisers, as they would not normally be used in isolation (Vieira et al., 2011). Secondary plasticisers are used to provide additional properties to the material, as well as some being used to provide cost savings (Vieira et al., 2011). The most used secondary plasticiser within the PVC industry is ESBO, due to its low cost and ability to provide additional stability to PVC (Buddhiranon et al., 2018).

2.3.5 Fillers

Fillers are materials added to PVC to lower the overall material cost. Fillers are divided into functional and non-functional fillers. Non-functional fillers are those used primarily to reduce the cost of a material, while functional fillers provide additional properties to the material. However, all fillers will influence the properties of a material. This needs to be considered when using fillers within PVC compound, especially when using them at high loadings (DeArmitt and Rothon, 2016). Properties likely to be influenced due to adding filler include the material's relative density, opacity, colour, and stability. Calcium carbonate is most widely used, followed by talc and kaolin clay.

2.3.5.1 Calcium Carbonate

As discussed, calcium carbonate is the most used filler in compound PVC. This material is mined from chalk, limestone, or marble quarries. Calcium carbonate filler is most often calcite, the most common and most stable form of calcium carbonate. Following mining calcium carbonate will be milled and then classified to a particular particle size range. The most used grade of calcium carbonate in compound PVC is industrial grade GCC, although higher grades of calcium carbonate may also be used to assist with processing, colour, and other material properties. A common issue with industrial grade GCC is a dirtier colour and issues with processing, as well as the occurrence of agglomerates, the latter resulting in poor distribution of the calcium carbonate. This can have an influence on the properties of the material, making the properties harder to predict. It is because of this that several different grades of GCC are available on the market, as outlined in Table 2-6. Whilst all the GCC materials are mined, coated GCC is mined, some GCC is coated in fatty acids, normally stearic acid (which converts to calcium stearate in the process). This results in a material that provides additional lubrication to the compound PVC, reducing the risk of any processing issues, as well as improving the material properties. PCC is made synthetically

from limestone, using a precipitation method. The precipitation method gives a much finer material and, in many cases, a different morphology, the less common aragonite. Each of these types of calcium carbonate results in differences to the properties and cost of the PVC compound, making it an important consideration during formulating the BOM.

Table 2-6: Table showing the different calcium carbonates used within the PVC industry, their particle size, brightness, and relative cost.

Calcium Carbonate Type	Particle Size D50 (mm)	Brightness (%)	Relative Cost	Purpose
Industrial grade GCC	3.1	81	£	Non-functional, used to lower the overall cost of the material.
Fine GCC	1.0	86	££	Provides cleaner finish and better dispersion.
Coated GCC	0.9	93	£££	Provides cleaner finish, improved dispersion, processibility and electrical properties.
PCC	0.1	96	££££	Provides cleaner finish, increased dispersion, gel speed, tensile strength, and elongation.

2.3.5.2 Other Fillers

There are several other fillers available on the market that do not use calcium carbonate, including, dolomite, talc, and calcined kaolin clays.

In this work industrial grade GCC will be used due to being the most used within GP pPVC.

2.3.6 Specialty Raw Materials

In addition to the raw materials already discussed, there are several other raw materials that can be used to provide additional properties that may be required for the end use of the material. Table 2-7 gives a selection of specialty raw material groups, alongside their purpose within PVC compound, and some common examples from the raw material group. Within GP pPVC these are not materials that are normally added as standard but are those that would be used if a customer specifically requests the property they provide. Each of these raw materials will have an impact on the overall cost of the material, this cost can vary significantly depending on the exact raw material used.

Table 2-7: Non-exhaustive list of specialty raw materials used in PVC and their purpose.

Additive Type	Purpose	Examples
Flame Retardants & Smoke Suppressants	Used to limit the spread of fire and smoke. Used for safety reasons in many applications, such as plastic floor matting used in commercial kitchens.	ATH, zinc borate, antimony trioxide.
UV Additives	Used to provide protection against sunlight, normally in external applications, such as window frames.	Titanium dioxide, benzophenones.
Antimicrobials	Normally categorised as antibacterial and antifungal, these prevent the growth of microbes on the surface of the plastic.	Zinc pyrithione, isothiazalinones, silver ions.
Blowing Agents	These are used to create foam products, which can improve the mechanical properties, as well as creating lightweight materials. Commonly used in footwear.	Organic acids, azodicarbonamide, sodium bicarbonate
Pigments	The most common of the specialty additives. Used to give PVC a specific colour/tone. Pigments can be used to hide the colour related effects of PVC degradation. Can be combined with resin or waxes to create a masterbatch.	Titanium dioxide, carbon black, copper phthalocyanine, dioxazine.

2.4 Preparation/Production

Compound PVC refers specifically to the gelled material created when the resin and other materials are melted and combined to produce a homogenous, dust free, conveyable product. There are subtle differences in the preparation technique used for full scale and laboratory production, which will be explored within this section.

2.4.1 Industry Preparation

Within the PVC industry, customers can purchase materials as either compound pellets or as a powder, referred to as a dry blend. A dry blend is when the material has been mixed to the point at which it has dried, liquid additives have been absorbed and the mix is homogenous. In both cases the dry blend must be created first, and then the pellets are produced from processing the dry blend with an extruder.

2.4.1.1 Mixing

The raw materials for the required PVC BOM are mixed in a high-speed mixer at elevated temperatures. The maximum temperature will be between 105°C and 125°C, depending on the application and the raw materials used. Some raw materials will be added at different temperatures, e.g., filler is added around 90°C - 95°C. If a high loading of filler is added too early, it can result in the material abrading the mixer, giving a grey tint to the

material. Mixing time is temperature dependant, and therefore varies between different mixture types. However, on an industrial plant in a commercial setting, it will be mixed for around 5 – 10 minutes, during which time it will meet the required temperature. Following mixing, the powdered mix will be dropped into a cooler to bring it down to around 30°C. The cooler, equipped with a water-cooled jacket, operates at a lower speed to prevent sticking and clumping in the mix. If the material is still hot once agitation stops, clumping can occur, causing delays in processing, either during pelletisation or with the customer as a dry blend. On a commercial scale the mixer will normally take 200 – 400 kg per mix. In some cases, raw materials will be added into the cooler. However, this is infrequent and only as a last resort if it cannot manage the higher temperatures in the high-speed mixer or to give a specific texture.

2.4.1.2 Compounding and Pelletisation

Dry blends can be sold as is or as a fused compound. Compounding is a process in which the powder goes from a mixture of various materials and becomes a solid, fused, plastic. This is completed using a specialised extrusion process. There are several distinctive designs and systems that can be used for this purpose.

The dry blend typically enters the extruder via the hopper where it gets carried down the barrel on a turning screw. As the material moves down the barrel, the heat, along with the shear from the screw turning, melts the dry blend. This creates molten compound PVC. As the screw turns, it also ensures that the non-melting raw materials are distributed through the molten PVC. Initially it is the heat and mixing that creates a tacky powder that gradually becomes molten, as it gets further down the barrel shear starts to have a larger impact. The barrel itself is normally divided into zones that can be heated individually, or that can also have different screw patterns. This configuration creates a heating zone, a compression zone, and a shear gap area. Each zone influences the way the molten PVC

behaves and ensures that the material reaches gelation and mixes homogeneously.

Once the molten PVC reaches the end of the barrel, it is forced into a narrow chamber and towards a die, which can have many different shapes and sizes. This die is often referred to as the “pepper pot” due to its resemblance to one. Depending on the size of the die and the job at hand, the head will be covered with holes between 1 – 3 mm. The molten PVC is pushed through these holes, creating strings of compound PVC, which are cut as they exit the die to form pellets. As the material is still molten at the point of being cut, it is important to cool them to ensure they do not stick to each other and to keep a regular shape. Once cooled (either air or water cooling), the pellets are bagged or stored in a silo until the customer's requested delivery date.

2.4.2 Laboratory Scale Preparation

It is not always possible to use or provide pellets within a laboratory environment; therefore, different preparation techniques are required to make samples. The two most common ways are using a two-roll mill and/or a two-stage mixer.

2.4.2.1 Two-Roll Mill

A two-roll mill has two rotating steel rolls that can be heated. Temperatures between 125°C - 200°C are typically used to process PVC. Figure 2-8 gives a diagram of the rollers and the material as it is being processed. Before using the mill, the gap between the rollers is set to the minimum value to ensure minimal loss of material. The raw materials are then placed into the feed zone and the rollers are switched on. The rollers rotate towards each other. This takes the material through the gap and as this happens, it gets tacky and small parts start to gel. At this stage, the roll gap can be adjusted to change the thickness of the hide. Once fully incorporated, the hide is removed and placed on a clean surface to cool.

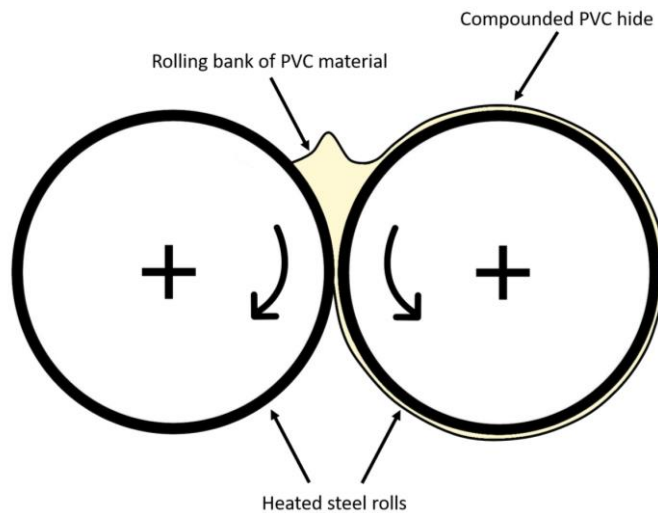


Figure 2-8: Diagram showing how a PVC hide is produced on a two-roll mill from individual raw materials.

2.4.2.2 Two-Stage Mixer

In laboratories a two-stage mixer can be used, these are lab-scale versions of those used in a production facility. A lab scale two-stage mixer works the same as that used on a compounding PVC plant (described and referenced in Section 2.4.1.1). The raw materials are added to the mixer and mixed until the desired temperature is reached. The mix is then released into the cooler and cooled at low speed until it reaches 30°C. The dry blend produced can then be extruded to create the compound PVC. Most laboratory scale extruders do not have the ability to pelletise the PVC compound.

There are several factors to be considered when considering the preparation techniques, and these are shown in the Table 2-8 below.

Table 2-8: Table showing the advantages and disadvantages of different preparation techniques within a PVC laboratory.

Technique	Two-Roll Mill	Two-Stage Mixer and Extrusion
Advantages	<p>Can produce material in 10 minutes (including weighing out). Once the material starts to gel you can instantly see differences with other materials. Can get a feel for the material whilst cross cutting and folding.</p>	<p>Comparable with plant mixing and compounding. Less risk of material being under gelled (important when testing mechanical properties). Includes two mixing processes so produces homogenous material.</p>
Disadvantages	<p>When completing multiple millings human error is more likely to occur due to monotony of the task. Due to cross cutting and folding, there can be a significant difference between each person's milling. Uses less material and therefore any weighing errors are more impactful.</p>	<p>For one mix it can take an hour (including weighing out, mixing, and cleaning), followed by at least 30 minutes to extrude. One can only observe major differences in material once it is being extruded. Uses more material and therefore more waste is produced.</p>

2.5 Testing of Compound PVC

PVC is tested at multiple stages during its life cycle, the majority of which occur during the development of a new products as well as during quality control and assurance. PVC compound may also be tested during its use and at the end of its life. Several types of tests can be performed, and the cocktail of tests depends on the desired properties and specific requirements of the end user.

Table 2-9 summarises the different tests typically conducted during the development of PVC compound, as well as the required technologist experience, duration, and raw material dependence associated with each test/analysis.

Table 2-9: Table outlining the tests commonly used within the PVC industry, with the stage at which this would normally be performed, the technologist experience requires, the main influencer, secondary influencer, the instrumentation requires, the test time, the conditioning time, property being tested, the PVC type and any standard that are followed.

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
Performed At What Stage (In General)	Development QC	Development	Development QC	Development QC	Development	Development QC	Development	Development	Development	Development
Technologist experience required	Low	Low	Low	Low	Medium	Medium	Low	Medium	Medium	Medium
Main Influencer	Plasticiser	Plasticiser	Filler	Stabiliser Package	Plasticiser/ Filler	Stabiliser Package/ Plasticiser	PVC Type	Plasticiser/ PVC Type	Stabiliser Package/PVC Type/ Plasticiser	Flame Retardant Additives
Secondary Influencer	Filler	Filler	Plasticiser	Some plasticisers	PVC type	Filler	Stabiliser Package	Stabiliser Package	Filler	Filler and Plasticiser
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)

2.5.1 Tests

This investigation focuses on pPVC. The tests/analyses typically associated with this type of polymer will be explored in this section.

2.5.2 Hardness and Softness Testing

Hardness and softness testing gives a numerical value to the flexibility of a material. The two most common types of hardness testing used within the PVC industry are Shore A hardness and BSS. Shore A hardness is measured on a scale of 0 – 100 with the hardness increasing with the number. PPVC normally has a value between 40 - 100. BSS gives values over one hundred, however, PPVC will mostly fall between 0 – 100. The softness and flexibility of a material increases with an increase of BSS number/value and a decrease in the Shore A hardness. The tests themselves work on similar principles. A pin is lowered onto a sample for a set duration of time. The resistance of the material against the pin during this time determines the material's softness/hardness.

The softness of a material is related to the plasticiser concentration, this is because the plasticiser fills the free space within the PVC compound and spreads the distance between the polymer chains. This results in a decrease in cross linking within the PVC compound and therefore more movement when the indenter is placed onto the sample. Other raw materials can also cause changes in the softness of the material, such as calcium carbonate. It is worth noting that the softness of a material will change over time. When heated, the softness will be higher for around 7 days following the heating, due to the breaking of the existing cross linking (which reform over time). There can also be additional hardening due to the loss of plasticiser over time as it is not chemically bonded to the PVC compound. It is because of this that the softness of a PVC material is tested on day seven in all published standards.

2.5.3 Relative Density

The relative density of a material is its density ratio to water. PVC compounds always have relative densities greater than 1.00 gcm⁻³, except PVC containing a blowing agent additive. These additives create a cell structure within the compound PVC which can trap air and decreasing the relative density. This allows the material to float.

The density of compound PVC is related to the density of the raw material used to create it. Therefore, the use of certain raw materials will have a greater influence than other raw materials. The relative density is calculated using the Archimedes principle to calculate the volume of the material, providing that its mass in air and its mass in a fluid are both known, as seen in Equation 2-1 (BSI, 1991a).

$$RD = \frac{\rho_{substance}}{\rho_{reference}}$$

(2-1)

Where:

RD = Relative Density

ρ_{substance} = Density of substance being tested

ρ_{reference} = Density of reference

2.5.4 Tensile Testing

Tensile testing is a used to assess a sample's mechanical properties, specifically tensile strength, and elongation at yield, by subjecting a sample to controlled tension until it fails. Tensile strength and elongation give information on both the formulation and processing of a PVC material. Essential for applications such as cables and gaskets. Samples are prepared to standard dimensions and subjected to a force at a constant rate in the tensile tester until it breaks. The maximum stress that the sample can withstand before breaking is defined as the tensile strength, and the elongation at yield is recorded.

Materials under strain can exhibit elastic and plastic deformation. Elastic deformation of a material is reversible, and the material will behave like a spring, i.e., it follows Hooke's law. Under this deformation, the stress/strain graph of the material will be linear. The gradient

of this graph is defined as the elastic modulus of the material. However, for flexible PVC this region is so small as to be unmeasurable under normal test conditions. Instead, the PVC sample will exhibit plastic deformation where there is a more complex relationship between stress and strain (BSI, 1976a).

The tensile properties can be tested using tensometer, which can allow for the calculation of the tensile strength and elongation at yield. The equation for calculating the tensile strength can be found in Equation 2-2, in which the tensile strength is calculated from the applied force divided by the cross-sectional area. Equation 2-3 shows the equation used for the calculation of the elongation at yield from the calculation of the change in length from the final length and change in length, divided by the original length.

$$\sigma = \frac{F}{A}$$

(2-2)

Where: $\sigma = \text{Tensile} = \frac{\text{Strength}}{\text{Stress}}$

$F = \text{Applied Force}$

$A = \text{Cross – sectional Area}$

$$\varepsilon = \frac{l-l_0}{l_0} \times 100$$

(2-3)

Where: $\varepsilon = \text{Elongation at yield}$

$l = \text{Final Length}$

$l_0 = \text{Original Length}$

2.5.5 Congo Red Heat Stability

The Congo red test is used to measure the heat stability of PVC and is usually conducted at either 180°C or 200°C. When PVC is heated, thermal degradation occurs (as outlined in Section 2.3.2), with the release of gaseous hydrochloric acid. This release of gaseous hydrochloric acid can be measured to determine the overall stability of the PVC compound. The Congo red heat stability is tested through the time taken for a colour change to occur

on indicator paper. The indicator paper will change colour from red to blue once the atmosphere within the test tube is saturated and the time, in minutes, taken for this change can therefore be used as a measure of the heat stability (BSI, 1991b).

2.5.6 Other Testing

Whilst the tests outlined above is the most common tests used for pPVC, there are numerous other tests that can be completed depending on the application of the material and the desired properties. Some of these tests are outlined in Table 2-9.

2.6 Spectroscopic Techniques

2.6.1 FT-IR Spectroscopy

Fourier Transform Infrared (FT-IR) spectroscopy is an essential analytical technique extensively used in both industry and academia. It works on the principle that molecules absorb infrared radiation at specific frequencies corresponding to the vibrational modes of their chemical bonds. When infrared light of varying wavelengths passes through a sample, certain wavelengths are absorbed, resulting in changes in the intensity of the transmitted light. These absorbed wavelengths correspond to the vibrational energy levels of the molecular bonds within the sample (Smith, 1999; Griffiths and de Haseth, 2007).

FT-IR spectra are characterised by peaks, each representing a specific vibrational mode within the molecule. The positions and intensities of these peaks provide insights into the functional groups present in the sample, thus revealing its chemical composition and structure. By comparing experimental spectra with reference spectra or databases, analysts can identify unknown compounds and assess sample purity, composition, and reaction progress (Stuart, 2004).

2.6.1.1 ATR FT-IR Spectroscopy

Attenuated Total Reflectance (ATR) FT-IR spectroscopy is a variation of traditional FT-IR spectroscopy that enhances the analysis of solid and liquid samples. In ATR spectroscopy,

the sample is placed in contact with a crystal with a high refractive index, such as diamond. When infrared light is directed through the crystal, it undergoes multiple internal reflections at the crystal-sample interface, leading to enhanced absorption by the sample. This technique is particularly useful in industry as it requires minimal sample preparation and can be performed in situ (Ramer and Lendl, 2013).

2.6.2 Raman Spectroscopy

Raman spectroscopy is another vital analytical technique used to study molecular vibrations and identify chemical compounds. Named after C.V. Raman, who discovered the Raman effect in 1928, this technique provides complementary information to FT-IR spectroscopy and is particularly valuable for the analysis of complex samples and materials (Long, 2002).

Raman spectroscopy is based on the Raman scattering phenomenon, which occurs when incident photons interact with molecules and undergo inelastic scattering. In this process, a small fraction of incident photons undergoes a change in energy due to interactions with the vibrational and rotational modes of the molecules. The energy shifts in the scattered photons correspond to the energy levels of the molecular vibrations, providing information about the chemical bonds and structure of the sample (Ferraro et al., 2003).

The Raman spectrum consists of peaks that represent the different vibrational modes within the molecule. Raman spectra often provide different vibrational information to FT-IR and can detect vibrational modes that are IR-inactive. While Raman spectroscopy is less commonly used than FT-IR, it finds wide application in fields such as pharmaceuticals, forensics, environmental science, and materials science. Its applications include the identification of polymorphs, analysis of biomolecules, detection of counterfeit drugs, and monitoring of chemical reactions (Das and Agrawal, 2011).

Chapter 3 will give an overview of the literature published during the last five years.

3. Literature Review

3.1 PVC Literature

As discussed in Chapter 2, PVC compound is one of the most used plastics in the world, with a wide range of applications from construction and packaging to healthcare and leisure. Naturally, this has resulted in PVC compound being the subject of numerous academic papers.

3.1.1 Literature Survey/Overview of the Literature

This literature review provides a comprehensive overview of the current knowledge on PVC compound, within academia. A literature survey was completed using Web of Science. The search terms 'PVC', 'poly vinyl chloride', and 'poly (vinyl chloride)' were used to collect the relevant papers from January 2018 to March 2023. In total 257 relevant articles were identified; these were then divided into the seven categories, described below, and defined by their main theme. The categories and determination of each was as follows:

Raw Materials – Articles which focused on a novel raw material being synthesised or an existing material repurposed for PVC compound.

Health and the Environment – Articles on PVC compound with the main theme being topics such as health, the environment, waste, and recycling.

Properties & Testing – Articles where the main purpose was to develop specific tests or determine the best existing raw materials for a specific property.

Applications – Articles where the main theme was the final application of the material used.

Modelling – Articles where the main theme was the creation of a model.

Reviews – All review articles covering assorted topics.

Other – Everything not categorised in the other six categories.

As can be seen in Figure 3-1 the percentages of each category were as follows; Raw Materials – 50%, Health & the Environment – 20%, Properties & Testing – 12%, Applications – 8%, Modelling – 6%, Reviews – 3%, Other – 1%.

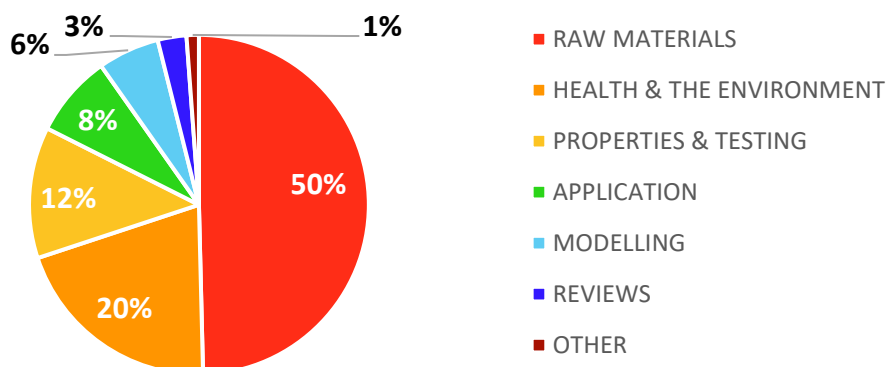


Figure 3-1: Pie chart showing the distribution of academic papers across the seven categories; Raw Materials, Health and the Environment, Properties and Testing, Application, Modelling, Reviews and Other.

Overall, this literature review aims to serve as a comprehensive introduction to the current state of knowledge on PVC compound. By understanding the current state of research on PVC compound, any gaps in the research can be highlighted.

3.1.2 PVC Raw Materials

As was found in the literature survey, 49% of the articles focused on the creation of novel raw materials for PVC compound. Within this category, further sub-categories can be identified, e.g., Plasticisers, Stabilisers, Composites, Fillers, Flame Retardants and Other Raw Materials. Figure 3-2 gives the percentages for each of the sub-categories within the literature for raw materials.

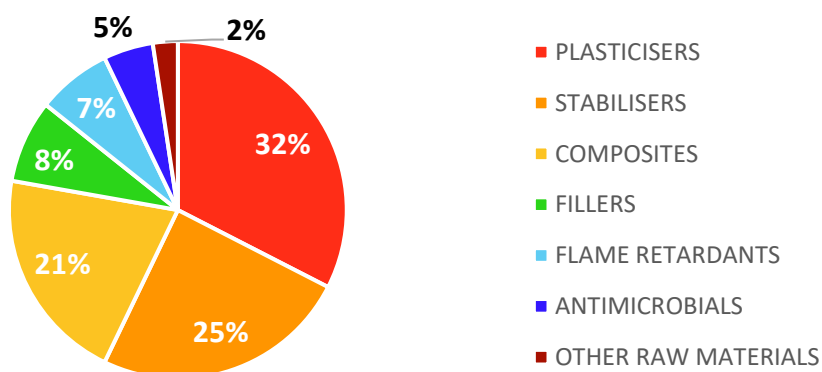


Figure 3-2: Pie chart showing the distribution of academic papers for the Raw Material category, sub-categorised into; Plasticisers, Stabilisers, Composites, Fillers, Flame Retardants, Antimicrobials, and Other Raw Materials.

Over half the papers released on raw materials in PVC compound are focused on plasticisers and stabilisers. This is likely, in part, due to these areas experiencing numerous legislative changes in the last decade, as well as being problematic areas from an environmental and health point of view.

3.1.2.1 Plasticisers

The focus of the academic research on plasticisers, within PVC compound, is the development of alternatives to traditional phthalate-based plasticisers. A substantial number of papers focused on the use of biobased plasticisers, such as cardanol and castor oil as alternatives to phthalate plasticisers (Deng et al., 2022; Greco et al., 2018; Satapathy and Palanisamy, 2021; Stolp et al., 2021; Zhu et al., 2021). Other research moved in a different direction, investigating the use of waste products from other industries to produce plasticisers. For example, Zheng et al (2018) investigated a more environmentally friendly plasticiser, produced from a waste cooking oil. These papers considering more sustainable plasticisers demonstrate that these novel plasticisers can provide similar or improved properties to phthalates and other common plasticisers, whilst also offering better environmental and health benefits. However, the commercial viability of these novel plasticisers was not investigated. It is worth noting that whilst success has been found with these more sustainable plasticisers, it is unlikely that any will be scaled up in their production in the short to mid-term.

Whilst most of the plasticisers discussed in the literature focused on creating less toxic, more sustainable plasticisers, the remaining papers investigated the improvement of the PVC compound's properties and the inclusion of additional properties. Several papers explored the improvement of the migration properties of the plasticiser, which in turn would provide a longer service life to the PVC compound (Aboghoniem et al., 2022; Gao et al., 2022; Mazitova et al., 2020; Sokolova et al., 2018; Zhu et al., 2021). Most found success

with these improvements. The improvement in service life would, inadvertently, provide environmental benefits due to a decrease in the need for replacement of the material in the future. As many of these improvements are based on existing raw materials, used within PVC compound, there is less concern regarding the commercial viability and therefore these changes are more likely to hit the market in the short term.

Overall, the literature suggests that new PVC plasticisers, such as plant oil-based alternatives, are being developed and tested as a response to concerns over the toxicity and environmental impact of traditional plasticisers. These new plasticisers offer promising alternatives that can provide similar or improved properties whilst also offering better safety and sustainability. However, as mentioned, it is unlikely that these raw materials will be available within the PVC compound industry within the short to mid-term.

3.1.2.2 Stabilisers

Of the 257 articles considered, 31 focused on novel stabilisers, which can be separated into those investigating thermal stabilisers (17), UV stabilisers (13) and one paper focused on gamma stabilisers.

The research into novel thermal stabilisers has an overall focus on moving away from the materials currently used, whether this is to gain increased performance, or for environmental reasons, such as the creation of less toxic stabilisers. Even when it is not the main aim of the research the environmental implications are frequently considered due to the current pressures on the polymer industry. When the focus of the research is the introduction of less toxic or more sustainable stabilisers, multiple angles have been considered. Marceneiro et al. (2022) considered natural based, solvent free calcium soaps from renewable sources and by products, such as eggshells. Similarly, Putrawan et al. (2022) aimed to produce novel calcium and zinc carboxylates from palm oil by-products. Both aimed to use existing waste streams to minimise the environmental impact. Verma

et al. (2019) aimed to remove/decrease the use of certain metals, within PVC compound, therefore decreasing the toxicity, by using organic stabilisers. This approach was also taken by Shi et al. (2022). Several papers investigated the use of LDH-based stabilisers, which would achieve the same outcome (Aisawa et al., 2019; Du et al., 2023; Guo et al., 2021; Shen et al., 2023). The use of LDH-based stabilisers was one of the most commonly occurring themes within the literature. LDH's are synthetic clays with hydrotalcite-like properties, which can be produced with multiple different structures and materials attached. This makes them extremely versatile for their use, allowing both existing and novel stabiliser technology to be combined with them to provide a synergistic effect.

Another theme that was identified in the literature was the use of rare earth metals as stabilisers (Liu et al., 2020; Wang et al., 2022; Xubo et al., 2022). Whilst promising results were found, there are still questions regarding the environmental implications of using rare earth metals for stabilisers, as well as their commercial viability.

As PVC resin requires stabiliser to be functional, it is easy to understand why there is such a push to find new thermal stabilisers that provide improved performance and improved environmental factors.

Of the papers on UV stabilisers, 9 investigated the use of tin (or other transition metal) based compounds to improve the UV stability of PVC compound. All the papers determined that the compounds studied provided some degree of UV stability, though with mixed success (Ahmed et al., 2020; Fadhil et al., 2022a; Fadhil et al., 2022b; Haddad et al., 2021; Mohammed et al., 2020; Mohammed et al., 2021; Mujbil et al., 2022; Naoom et al., 2022). The remaining four papers on UV stabilisers investigated the development of novel, organic-based UV stabilisers, all demonstrating some success when tested (Al-Mashhadani et al., 2022; Farhan et al., 2022; Mohamed et al., 2023; Salman et al., 2018).

When considering UV stabilisers, there was little focus on the environment and

sustainability, unlike what has been seen so far with the raw materials considered. Whilst the exact reason for this is unknown, there are several potential causes for this. UV stabilisers are only used in materials that will be experience long term exposure to the sun, and this significantly limits the use of UV stabilisers to PVC compound used for external applications. This means that their use is limited, and the demand is low therefore it is not deemed as worthwhile researching more sustainable alternatives. Another potential reason could be that the use of UV stabilisers can significantly prolong the service life of PVC compound, therefore minimising the overall environmental impact.

Finally, Da Silva et al (2019), investigated the use of vegetable oil from coffee grounds for the creation of a novel gamma stabilisers. The results demonstrated promising radioprotection; however, the commercial viability was not investigated.

Overall, the research into PVC stabilisers is varied, and considers different stabiliser types, providing different advantages. There are some common themes present, including a focus on the sustainability of thermal stabilisers. As was seen with the literature on plasticisers, little consideration has been shown for the scaling up and commercialisation of these novel stabilisers, deeming them unlikely to be commercialised in the short term, and only rendering them solutions for the long term.

3.1.2.3 Composites

PVC composites are materials made by combining PVC with other materials to provide added properties. Research has focused on developing new composites that can provide enhanced properties. 13 papers on composites investigate the use of nanocomposites.

The nanocomposites used within PVC compound, are made by adding low levels of a nanomaterial to PVC compound. Examples include organoclays, graphene and metal oxides. The literature on nanocomposites within PVC compound reports increases in the mechanical properties, with many reporting increases in the migration properties,

dielectric properties, and even in antimicrobial activity (Abdel-Gawad et al., 2019; Abdel-Gawad et al., 2020; Allahbakhsh, 2020; Barghamadi et al., 2019; Beygi et al., 2022; Ibrahim et al., 2023; Ibrahim et al., 2023; Nikam Pravin et al., 2018; Sayed et al., 2022; Yang et al., 2023). Of the research around the use of nanocomposites within PVC compound few addressed the commercial viability or the concerns regarding environmental and financial implications. The high cost of nanomaterials significantly limits their use within the industry, where the number one driver for most raw material choices is cost.

The research on PVC composites that did not utilise nanomaterials was extremely varied, with other polymers, such as polystyrene, being considered (Tourta, 2022) to novel copper compounds (Ahmed et al., 2021; Yousif Emad et al., 2019). Whilst there was significant variation with the composites being produced, most aimed to improve the mechanical properties or the photostability of the material, therefore improving the material longevity (Abed et al., 2021; Ay and Yenil, 2021; Hammiche et al., 2021; Li et al., 2022; Liu et al., 2020; Solovyeva et al., 2022; Wang et al., 2023; Yousif et al., 2019).

Overall, the literature suggested that new PVC composites are being developed and tested in response to increased lifetime performance and therefore improved sustainability, through the reduction of plastic waste. However, before novel PVC composites or PVC composites with nanomaterials can be introduced to the market, further research is required to ensure that these are commercially viable, as well as ensuring that any potential environmental concerns are addressed.

3.1.2.4 Fillers

Whilst fillers are commonly used within PVC compound, the research into novel fillers is limited. This is in part because the most common function of fillers is to reduce the overall cost of the material. The ten papers investigating novel fillers could be divided into those

that aimed to provide functionality to the filler, and those that are by products of other processes and therefore provide cost savings, alongside environmental benefits.

Liang et al. (2022) and Schlickmann (2019) reported the modification of calcium carbonate to create fillers that gave functionality to PVC compound without a need to investigate the compatibility in the matrix, as calcium carbonate is already the primary filler used within PVC compound. This would allow the improvements to PVC compound to be utilised on a commercial scale faster, as less work would be needed to prove that there are no long-term issues with the new material.

Waste materials researched included chicken eggshells (Khaleghi, 2021), corncob flour (Roman et al., 2020) and bagasse fibres (Youssef et al., 2022). Whilst improved mechanical properties were cited by all using waste materials, Roman et al saw significant changes to the flow properties. A change in the flow properties can be a significant issue as specific flow properties are a requirement for a well-functioning production line; therefore, it can take time and money to account for any changes to these properties.

Overall, the limited literature found suggests that novel PVC fillers are being developed that provide an improvement to either the mechanical properties and/or the thermal properties, both of which improve the longevity of the material. However, as has been discussed, further research and trials would be required to ensure that the financial and environmental implications are minimised.

3.1.2.5 Flame Retardants, Antimicrobials and Other Raw Materials

The remaining raw material research included novel flame retardants, antimicrobials, and two papers focusing on other raw materials. As this thesis is considering GP materials and these are very niche additives, a summary will not be provided.

3.1.2.6 Raw Material Conclusion

The main themes on raw material research are sustainability and the environmental

impact. This is not surprising; the current climate surrounding plastics and plastic waste is overall negative. This combined with the numerous legislative changes over the last decade mean that research into alternative raw materials is required more than ever.

A focus to make property improvements can also be seen, with migration resistance, UV stability and mechanical properties being investigated. An increase in any of these properties can have a direct impact on the service life of the material, in turn lowering its environmental impact.

3.1.3 Health and the Environment

In recent years, the climate surrounding plastics and their potential impacts on both human health and the environment has become increasingly negative. This is reflected within the literature, with 20% of the literature focusing on this subject. This was divided into three sub-categories: the environment, health, and waste and recycling. These are defined by: Environment – Papers that focus on the environmental issues relating to PVC compound, such as those investigating emissions and microplastics.

Health – Papers describing the effects of PVC compound and its raw materials on human health.

Waste and Recycling – Papers that consider alternative uses for waste PVC compound other than landfilling.

3.1.3.1 Environment

The literature surrounding PVC and the environment focused on the presence of microplastics within the environment, emissions of volatiles from PVC, and sustainability. Of the 14 papers about environmental issues, 8 of them focused on microplastics investigating the biodegradation of microplastics (Rad et al., 2022), the separation of microplastics (Zhang et al., 2023; Zhang et al., 2022), their interactions with their environment and the associated risk (Bao et al., 2021; Hummel et al., 2021; Mehmood et

al., 2022; Pedà et al., 2022), and their creation (Qin et al., 2022).

Other papers within the environment sub-category included three investigations into emissions from PVC compound, such as phthalate emission over time, as investigated by Castagnoli et al. (2019) and Gilliam et al. (2022). Noguchi et al. (2020) described the emissions from various polymers overtime, finding that PVC compound produced higher emissions than the other polymers investigated.

The final two papers investigate the sustainability of buildings, in line with associated legislation, as was done by Everard and Blume (2020) and Sevenster et al. (2019).

Overall, the investigations into the environmental affects surrounding PVC compound demonstrate that there is a lot of concern regarding microplastics and their effect on the environment, as well as highlighting the issues surrounding emissions from PVC compound once in the final product. The papers found in this sub-category suggest that there is concern regarding the environment and a push to find answers and therefore solutions.

3.1.3.2 Health

In total, 12 papers were published related to the human health aspect of PVC compound, investigating the interactions of raw materials on the human body from medical devices, food and food packaging, water systems, and toys.

Half of the papers within this sub-category investigated DEHP exposure from medical devices (blood bags, tubing, connectors, instrumentation, etc.). Whilst DEHP has been restricted for use within Europe since 2015, its use is still permitted for certain medical devices, such as blood bags and therefore there is still a risk of exposure to DEHP within the health sector. Five papers studying DEHP in medical devices focused on the potential exposure to DEHP and the associated risk (Bernard et al., 2021; Duarte et al., 2021; Haned et al., 2018; Kambia et al., 2021; Lautraite et al., 2022). All five studies found that DEHP migrates out of the medical devices, and all found that this did in fact pose a risk. Although

the risk to healthy adults is low, it is not negligible, whereas the risk to neonatal infants was found to be high and of great concern. Almeida et al. (2022) and Kambia et al. (2021) made comparisons between DEHP and other plasticiser options, determining that viable alternatives are available and less toxic. Kambia et al. suggests that DOTP can be used as an alternative as it is already widely used, decreasing the time to market for the product. DEHP and phthalates were also considered in other products, such as children's toys (Oteef and Elhassan, 2022) and flooring (Kim et al., 2023), both determining that due to children's behaviour, such as putting items in their mouth and crawling across the floor, put them at higher risk of phthalate exposure.

Food packaging has been an area of concern for phthalate exposure for several years. Carlos et al. (2018) determined that there are several alternatives to phthalates for food packaging following a report that food contributed to 10% of phthalate exposure. The same research group further investigated phthalates in food packaging, determining that phthalate exposure from fast food packaging was limited (Carlos et al., 2021).

The final two papers within this sub-category investigated other raw materials, with the exposure to fire-derived contaminants from PVC piping (Chong et al., 2019) and the risk of exposure to chlorinated paraffins both being considered (Yu et al., 2023).

As can be seen, when assessing the papers related to human health, the biggest concerns are those surrounding the presence of DEHP in medical devices. This is expected as DEHP has been restricted in its use due to being an endocrine disruptor, however, this is not as heavily restricted within medical devices.

3.1.3.3 Waste and Recycling

The final papers in this section related to the waste and recycling of PVC compound. In recent years there has been significant concern regarding plastic within the environment, as was seen in Section 3.1.3.1, and several investigations have been completed surrounding

microplastics. In combination with this, there is also a large amount of concern regarding the high levels of plastic waste within the ocean that is not biodegradable. Therefore, it is no surprise that 26 papers have been produced regarding PVC waste and recycling. The research into PVC waste and recycling is broad, with some considering the degradation of PVC, others describing the dichlorination of PVC and still others investigating how PVC waste could be used in a more efficient way rather than just as waste. Examples of recycling includes Assefa and Fieser (2023) who focused on the upcycling of PVC to polyethylene Co-styrene, Gohatre et al. (2021) who used rubber blends to enhance the properties of recycled PVC, and Li et al. (2021) who used waste plastic to obtain thermal cracking features. Interestingly only two of the papers found specifically looked at the characterisation and composition of PVC. These included one by Hamidi (2020) and another by Gohatre et al. (2020). Gohatre et al. (2020) used FT-IR to determine that a substantial portion of electrical cable waste was PVC compound. The study concluded, after additional testing, that the waste could be recycled into virgin PVC compound, and that further work was required due to the presence of the metal wire. Hamidi (2020) used GPC-SEC to characterise PVC materials recovered from post-consumer pipe. Using a THF extraction they were able to recover PVC resin that would be usable in the manufacture of PVC compound. However, the large-scale viability was not considered.

The papers found from the recycling and waste sub-category suggests that little is being done in terms of determining the composition of the waste, other than in the two scenarios described. This is an area in which a predictive model could potentially provide some insight into the waste being produced and whether it can be recycled into new PVC formulations. However, there is a clear direction towards finding viable solutions for waste to minimise the impact on the planet.

3.1.3.4 Health and the Environment Conclusions

When considering the publications surrounding PVC compound, and Health and the Environment, one can see there are significant issues regarding concern over plastics and PVC compound. In future, it is likely that there will be an increase in the research being completed within this area as the issues are truly relevant within the world at present.

3.1.4 PVC Properties and Testing

PVC compound is used due to its possessing of numerous different properties and its variability. This section aims to describe the properties and testing of PVC compound within the literature. In the period investigated, 31 articles have been published relating to the properties and testing of PVC. Within these papers a wide range of techniques have been used to determine various properties of PVC. These can be split into analytical testing, mechanical/rheological and other tests.

3.1.4.1 Analytical Testing

Of the 31 papers found, 10 investigated the use of analytical techniques to determine raw materials or properties of PVC compound. The most used technique was infrared, primarily ATR-FT-IR. Other commonly used techniques included Raman spectroscopy, NMR, DSC and TGA. Despite only a handful of techniques being used, the research is varied with the techniques being used in different combinations on several types of PVC to determine different properties.

Within these ten papers, some chose to focus on niche subjects, e.g., two of the papers found used FT-IR as a non-invasive technique to identify plastics within heritage items (Committee, 2018; Rosi et al., 2021). Waheed et al. (2023) developed a method to use NMR to detect and quantify phthalates within toys made from PVC compound. Yakes et al. (2022) also investigated a niche application, by determining the presence of phthalates in dairy tubing, using portable vibrational spectroscopies, due to the dairy industry coming

under scrutiny for the presence of phthalates in dairy products. Mandrile et al. (2020) used surface enhanced Raman spectroscopy to identify organotin migrating out of food packaging. Each of these studies aimed to resolve a problem within a specific industry.

Irvin et al. (2022) aimed to provide a much broader application, using FT-IR spectroscopy and Raman spectroscopy to successfully quantify the DOTP and calcium carbonate concentrations in pPVC. Others used NMR to quantify plasticisers or UV stabilisers within PVC compound (Al-Mashhadani et al., 2021; Duchowny et al., 2022). In one study TGA was used to measure the stability of uPVC over a three-month period to allow PVC compound producers the ability to change their stabilisation for different climates (Amar et al., 2019). Li et al. (2021) used analytical techniques to assess the processing and mixing of PVC compound, providing useful information regarding the best procedures based upon the glass transition temperature.

Overall, analytical testing is utilised for many varied reasons within the literature, for both extremely specific, niche problems, to broader applications. Irvin et al. (2022) are the only ones who have utilised techniques to detect more than one raw material, the other papers all focused on a specific property or raw material.

3.1.4.2 Mechanical & Rheological Testing

Ten papers focused on the mechanical and rheological properties of PVC compounds. Nine of these papers investigated the properties of uPVC, with three determining various mechanical/rheological properties of blown/foamed uPVC (Nerkar, 2023; Yao et al., 2022; Zhou et al., 2023). The remaining six (on uPVC) studied the influence of different raw materials and processing factors on uPVC (Abd El-Hakim et al., 2021; Demirci et al., 2019; Frank et al., 2021; Jiang et al., 2018; Nerkar et al., 2023; Wang et al., 2023). These papers, whilst providing interesting information, all focused-on uPVC rather than pPVC.

The remaining paper within with in this sub-category used pPVC. Marceneiro et al. (2018)

investigated the relationship between morphological properties and the rheological and ageing properties of the pPVC, finding that traditional plasticisers offer more favourable interactions with PVC when compared with non-conventional plasticisers.

Overall, this demonstrates the papers on mechanical and rheological properties are mostly focused on uPVC and presently there are no papers considering GP pPVC.

3.1.4.3 Other Testing

The remaining ten papers focused on several different things, such as, dehydrochlorination, chemical resistance and migration testing.

3.1.4.4 Properties and Testing Conclusion

The papers within this category cover a wide range of properties and testing, however clear gaps are evident. The papers all tend to focus on one raw material type, or one property, rather than looking at the relationships between multiple raw materials or multiple properties. This is a gap in the research, due to the sheer amount of information that could be discussed if it were not focused on these singular subjects.

3.1.5 Applications

The remaining 8% of articles focused on the applications of PVC. Further categorised into construction, 3D printing, cables and electrical, food and other applications.

3.1.5.1 Construction

Seven papers investigated the use of PVC for the construction industry. Three of these were for flooring applications, all three focused on how they were able to improve flooring materials, to make them more future proof. The papers looked at improvements for health care facilities (Gotlib et al., 2019); improvements to the water resistance (Mario et al., 2019) and using alternative plasticisers to decrease plasticiser migration and extend the product life (Sokolova et al., 2018). The remaining two papers looked at the use of

nanocomposites, such as PVC/calcium carbonate for construction materials (Malak et al., 2022) and the use of PVC to provide corrosion resistance to slopes (Yong-gang et al., 2022).

3.1.5.2 3D Printing

In recent years, the interest in 3D printing has increased dramatically as it allows for faster and more cost-effective fabrication of complex articles. Four papers investigated this, exploring the shape memory and shape recovery of 3D printed PVC (Aberoumand et al., 2023; Calafel et al., 2020; Rahmatabadi et al., 2023; Ranjan et al., 2021).

3.1.5.3 Cables and Electrical

PVC compound is one of the most used polymers for wires and cables, it is therefore no surprise that there are papers looking at this application. Whilst Geng et al. (2022) investigated the use of PVC composite for dielectric films for capacitors, whereas the remaining two papers (Kemari et al., 2018; Soler et al., 2018) completed investigations into the improvements of cables in specific applications.

3.1.5.4 Flame Retardant Materials

The use of polymers in various applications has called for the need of flame retardant, three papers investigated enhancing the flame retardancy in specific applications, such as foams and wood composites (Elnaggar et al., 2019; Fang et al., 2022; Zhang et al., 2019).

3.1.5.5 Other

The final five papers regarding applications looked at various subjects which were industrial calendaring (Jamarani et al., 2021), proton exchange membranes for fuel cells (Liu et al., 2021), cargo screen applications (Park et al., 2019), magnetic tapes for audio heritage (Ribeiro et al., 2019) and museum showcase construction (Samide and Smith, 2022).

3.1.5.6 Application Conclusion

As can be seen in this section PVC compound can be used across numerous applications, with new research being completed each year. Most the research completed focused on the improvement of the materials already used in the application.

3.1.6 PVC Models

Fifteen of the papers found used some form of computational model. Three of these papers were for the specific prediction of the formulation of PVC for cables, accounting for the addition of additives such as LDH's (Cherfi et al., 2023; Fechter et al., 2019a; Fechter et al., 2019b). Whilst these papers have created models to predict the formulations of PVC compound, they are focused on such a specific application, and it would take work to develop this into a model that could be utilised for GP PVC.

Six papers investigated the use of predictive models for the prediction and understanding of the thermal degradation of PVC (Demir and Ulutan, 2018; Huang et al., 2018; Kuznetsov et al., 2022; Li and Liu, 2022; Papanikolaou et al., 2023; Wang et al., 2022). Kuznetsov et al, (2022) used Raman spectroscopy to assess the degradation of the polyene, by modelling the polyene length versus the wavenumber found from Raman spectroscopy.

The final six papers utilising modelling with PVC investigated the modelling of gel actuators (Al-Rubaiai et al., 2022), exposure to phthalates (Gkrillas et al., 2021), Bond dissociation enthalpies (Huang et al., 2018), photochlorination of PVC (Maity et al., 2023), Migration studies (Mercea et al., 2021) and the pyrolysis and carbonisation of PVC (Tian et al., 2021).

3.1.6.1 PVC Models Conclusions

Whilst there are fifteen papers that utilise models for PVC compound, only three aimed to create formulations, based on the required properties, focusing on a specific application. One paper utilised spectroscopy to create a model, however this was to investigate the degradation of the PVC, rather than to predict the raw material concentration.

3.1.7 Reviews

Seven papers were review articles describing various aspects of PVC, including a review of the history of PVC (Mijangos et al., 2023), a review on materials replacing commonly used plasticisers (Czogala et al., 2021), a review of reactive plasticisers (Bodaghi, 2020), a review of the work completed surrounding PVC and 3D printing (Randhawa et al., 2021), a review of the key additives of polymers (Allen and Edge, 2021), a review on olive stones as a filler for polymers (Valvez et al., 2021) and overview of test methods and European Union regulatory status surrounding smoke acidity (Sarti, 2022).

3.1.8 Other

Three papers did not fall into the other categories and investigated things that no other papers were considering. One paper focused on die design for PVC processing (Tomassini, 2018), one investigated hydrothermal carbonisation of PVC (Zhang et al., 2022) and one investigated the removal of methylene blue from PVC compound (Jagodić et al., 2022).

3.2 Conclusions

This literature review has demonstrated that a lot of research has been completed around PVC compound, the majority of which investigated the raw materials used within PVC compound. There is a gap within the knowledge when considering PVC models and the characterisation of PVC compound using spectroscopic techniques. As has been demonstrated within other industries, the use of models can significantly speed up processes and therefore increase overall production times, profit, and customer satisfaction.

A model that utilises spectroscopic techniques to characterise both the raw materials and properties of PVC could provide significant changes to how the industry operates and contribute to the current knowledge surrounding PVC compound. Companies in the polymer industry willing to adopt and apply the POLEMERS model created in this

investigation, will undoubtedly reap significant benefits in terms of product development and customer satisfaction.

Chapter 4 describes the experimental component of this investigation.

4. Methodology

Chapter 4 outlines the procedures completed to produce and test all the samples required.

4.1 Sample Preparation

The first step was to produce pPVC samples with varying concentrations of raw materials as well as using different preparation techniques to assess their performance properties and/or spectroscopic data against each other. This is described in Phase 1 and Phase 2. For this purpose, typical pPVC raw materials were chosen, K70 PVC resin, DOTP plasticiser, GCC filler and a calcium zinc stabiliser. It is followed by the description of phase 3 samples; wherein several types of raw materials are considered in the same way.

4.1.1 Phase 1

In Phase 1, 36 formulations with varying concentrations of DOTP plasticiser and GCC filler and constant levels of K70 resin and a calcium-zinc stabiliser package were characterised and tested.

Samples were prepared in a standard industry laboratory method, using a two-roll mill. The samples were weighed out, in grams, to two decimal places, into a plastic beaker, where they were gently combined with a palette knife for 30 seconds, before being compounded using a 6" x 13" Farrel Two-Roll Mill. The roll temperature was set to 155 - 160°C, the front roll speed was set to 25.5 rpm and back roll speed was set to 34.0 rpm. After being placed on the rolls the samples were mixed for 6 minutes with crosscut and fold back being performed every 10 seconds throughout this process allowing for a fused hide to be produced. Hides were then placed on a clean, stainless-steel sheet to cool.

Samples were then prepared in accordance with the relevant standards as outlined in Section 4.2. Test plaques were compression moulded using a Neoplast HYD 30T hydraulic press and mould sizes as outlined for each sample below. Samples were held at a

temperature of 170°C and a pressure of 150 bar on an automated cycle for 5 minutes before being cooled within the press for a further 8 minutes on a cold-water cycle. Appropriate test pieces were cut using a RayRan compressed air sample cutter with the appropriate cutting tool or with a freestanding band saw.

Table 4-1: Table of PVC compound BOMs for Phase 1, with varying concentrations of DOTP plasticiser and GCC filler.

Sample ID	PVC Resin (PHR)	DOTP Plasticiser (PHR)	GCC Filler (PHR)	Stabiliser Package (PHR)
001	100.00	0.00	0.00	2.25
003	100.00	20.00	0.00	2.25
005	100.00	40.00	0.00	2.25
007	100.00	60.00	0.00	2.25
009	100.00	80.00	0.00	2.25
011	100.00	100.00	0.00	2.25
023	100.00	0.00	20.00	2.25
025	100.00	20.00	20.00	2.25
027	100.00	40.00	20.00	2.25
029	100.00	60.00	20.00	2.25
031	100.00	80.00	20.00	2.25
033	100.00	100.00	20.00	2.25
045	100.00	0.00	40.00	2.25
047	100.00	20.00	40.00	2.25
049	100.00	40.00	40.00	2.25
051	100.00	60.00	40.00	2.25
053	100.00	80.00	40.00	2.25
055	100.00	100.00	40.00	2.25
067	100.00	0.00	60.00	2.25
069	100.00	20.00	60.00	2.25
071	100.00	40.00	60.00	2.25
073	100.00	60.00	60.00	2.25
075	100.00	80.00	60.00	2.25
077	100.00	100.00	60.00	2.25
089	100.00	0.00	80.00	2.25
091	100.00	20.00	80.00	2.25
093	100.00	40.00	80.00	2.25
095	100.00	60.00	80.00	2.25
097	100.00	80.00	80.00	2.25
099	100.00	100.00	80.00	2.25
111	100.00	0.00	100.00	2.25
113	100.00	20.00	100.00	2.25
115	100.00	40.00	100.00	2.25
117	100.00	60.00	100.00	2.25
119	100.00	80.00	100.00	2.25
121	100.00	100.00	100.00	2.25

4.1.2 Phase 2 & 3

For Phases 2 and 3 a further 60 formulations, shown in Table 4-2 and Table 4-3, were evaluated. The 25 formulations created in Phase 2 had varying concentrations of DOTP plasticiser and GCC filler, along with K70 resin and a stabiliser package. The 35 formulations

created in Phase 3 had variations in the plasticiser type, filler type, resin type, as well as the stabiliser package concentration. Note: Samples 226 – 240 were mixed alongside Phase 2 but have been included with Phase 3.

Table 4-2: Table containing PVC compound formulations selected for Phase 2.

Sample ID	K70 PVC Resin (PHR)	DOTP Plasticiser (PHR)	GCC Filler (PHR)	Stabiliser Package (PHR)
201	100	0	0	2.25
202	100	25	0	2.25
203	100	50	0	2.25
204	100	75	0	2.25
205	100	100	0	2.25
206	100	0	25	2.25
207	100	25	25	2.25
208	100	50	25	2.25
209	100	75	25	2.25
210	100	100	25	2.25
211	100	0	50	2.25
212	100	25	50	2.25
213	100	50	50	2.25
214	100	75	50	2.25
215	100	100	50	2.25
216	100	0	75	2.25
217	100	25	75	2.25
218	100	50	75	2.25
219	100	75	75	2.25
220	100	100	75	2.25
221	100	0	100	2.25
222	100	25	100	2.25
223	100	50	100	2.25
224	100	75	100	2.25
225	100	100	100	2.25

The samples for Phases 2 & 3 were made using a 2-stage mixer instead of using a two-roll mill to better replicate the process of producing PVC compound on an industrial scale. This process also allowed a comparison between preparation techniques to be completed. Sample preparation is as follows. Samples were weighed out, in grams, to 2 decimal places. All the raw materials, except the calcium carbonate filler, were added to the high-speed mixer (stage 1) mixed at 1600 rpm until the mixer reached a temperature of 95°C. If filler was required the mixer was stopped, opened and the filler added before the mixing was restarted and allowed to continue until the mix reached 115°C. Once the mixture reached

115°C, it was stopped and dropped into a cooler and span at 400 rpm until it reached a temperature of 35°C (stage 2), at which point it was dispensed into bags and stored for 24 hours before any further processing was completed. Before the first mix each day is completed a warmup mixture is completed to get the mixer up to running temperature to ensure a more consistent mixing in each test mix.

Following the 24-hour rest time the samples were run through a Haake Twin-Screw Extruder with a 50 mm x 2 mm strip die, at 165°C across all four zones and 40 rpm to ensure adequate mixing. Ten 300 mm strips were collected for each sample.

Following extrusion, samples were prepared in accordance with the relevant standards as outlined Section 4.2. Test plaques were compression moulded using a Neoplast HYD 30T hydraulic press and mould sizes as outlined for each sample below. Samples were held at a temperature of 170°C and a pressure of 150 bar on an automated cycle for 5 minutes before being cooled within the press for a further 8 minutes on a cold-water cycle. Appropriate test pieces were cut using a RayRan compressed air sample cutter with an appropriate cutting tool or with a freestanding band saw (dependant on the sample and test pieces required).

Table 4-3: Table containing PVC compound formulations selected for Phase 3.

Sample ID	K70 PVC Resin (PHR)	DOTP Plasticiser (PHR)	DINP Plasticiser (PHR)	ESBO Plasticiser (PHR)	GCC Filler (PHR)	Stabiliser Package (PHR)	K66 PVC Resin (PHR)	K80 PVC Resin (PHR)	K100 PVC Resin (PHR)	Fine GCC Filler (PHR)	Coated GCC Filler (PHR)	PCC Filler (PHR)
226	100	45	0	5	25	2.25	0	0	0	0	0	0
227	100	40	0	10	25	2.25	0	0	0	0	0	0
228	100	25	0	25	25	2.25	0	0	0	0	0	0
229	100	0	0	50	25	2.25	0	0	0	0	0	0
230	100	50	0	0	25	1	0	0	0	0	0	0
231	100	50	0	0	25	2	0	0	0	0	0	0
232	100	50	0	0	25	3	0	0	0	0	0	0
233	100	50	0	0	25	4	0	0	0	0	0	0
234	100	50	0	0	25	5	0	0	0	0	0	0
235	0	50	0	0	25	2.25	100	0	0	0	0	0
236	0	50	0	0	25	2.25	0	100	0	0	0	0
237	0	50	0	0	25	2.25	0	0	100	0	0	0
238	100	50	0	0	0	2.25	0	0	0	25	0	0
239	100	50	0	0	0	2.25	0	0	0	0	25	0
240	100	50	0	0	0	2.25	0	0	0	0	0	25
301	100	45	0	5	0	2.25	0	0	0	0	0	0
302	100	45	0	5	25	2.25	0	0	0	0	0	0
303	100	45	0	5	50	2.25	0	0	0	0	0	0
304	100	45	0	5	75	2.25	0	0	0	0	0	0
305	100	45	0	5	100	2.25	0	0	0	0	0	0
306	100	20	0	5	0	2.25	0	0	0	0	0	0
307	100	70	0	5	0	2.25	0	0	0	0	0	0
308	100	95	0	5	0	2.25	0	0	0	0	0	0
309	100	0	25	0	0	2.25	0	0	0	0	0	0
310	100	0	50	0	0	2.25	0	0	0	0	0	0
311	100	0	75	0	0	2.25	0	0	0	0	0	0
312	100	0	100	0	0	2.25	0	0	0	0	0	0
313	0	25	0	0	0	2.25	0	0	100	0	0	0
314	0	50	0	0	0	2.25	0	0	100	0	0	0
315	0	75	0	0	0	2.25	0	0	100	0	0	0
316	0	100	0	0	0	2.25	0	0	100	0	0	0
317	100	50	0	0	0	2.25	0	0	0	0	0	25
318	100	50	0	0	0	2.25	0	0	0	0	0	50
319	100	50	0	0	0	2.25	0	0	0	0	0	75
320	100	50	0	0	0	2.25	0	0	0	0	0	100

4.1.3 Phase 4

A final phase of 10 samples was prepared for verification of the model, as outlined in Table 4-4. These samples had varying concentrations of DOTP plasticiser and GCC filler to evaluate the main function of the model.

Table 4-4: Table containing PVC compound formulations selected for Phase 4.

Sample ID	K70 PVC Resin (PHR)	DOTP Plasticiser (PHR)	GCC Filler (PHR)	Stabiliser Package (PHR)
401	100	40	20	2.25
402	100	80	40	2.25
403	100	100	60	2.25
404	100	25	25	2.25
405	100	25	35	2.25
406	100	35	25	2.25
407	100	50	50	2.25
408	100	50	65	2.25
409	100	65	50	2.25
410	100	75	25	2.25

Samples were weighed out to two decimal places, into a plastic beaker, where they were gently combined with a palette knife, before being compounded using a 6'' x 13'' Farrel Two-Roll Mill. The roll temperature was set to 155 - 160°C, the front roll speed was set to 25.5 rpm and back roll speed was set to 34.0 rpm. After being placed on the rolls the samples were mixed for 6 minutes with crosscut and fold back being performed every 10 seconds throughout this process allowing for a fused hide to be produced. Hides were then placed on a clean, stainless-steel sheet to cool.

4.2 Industrial Testing

Samples were tested for their physical properties, as well as their spectroscopic fingerprint.

4.2.1 British Standard Softness

Samples for BSS testing were prepared using a 100 mm x 100 mm x 10 mm mould and were compression moulded using a Neoplast HYD 30T hydraulic press. Samples were tested for BSS using a variation of BS2782-3-365A (BSI, 1976b). The samples were tested 7 days following their production using a Wallace Cogenix Dead Load Hardness tester. Ten spots were tested from across each sample.

4.2.2 Shore A Hardness

Samples for Shore A testing were prepared as described in Section 4.1 using a 100 mm x 100 mm x 8 mm mould and were compression moulded using a Neoplast HYD 30T hydraulic press. Samples were tested for Shore A hardness (15) using a variation of BS EN ISO 868 (BSI, 2003). The samples were tested 7 days following their production using a Shore Instruments and MFG Durometer Type A tester. Ten spots were tested from each sample.

4.2.3 Relative Density

Samples for relative density testing were prepared as described in Section 2.1 using a 100 mm x 100 mm x 10 mm mould and were compression moulded using a Neoplast HYD 30T hydraulic press. To assess the relative density these plaques were then cut to produce five 25 mm x 25 mm samples. Relative density was determined using a variation of BS 2782-6-620A-620D (BSI, 1991a) using Ultratest D22 Densimeter.

4.2.4 Congo Red Heat Stability

Congo Red testing was completed using an in-house variation of BS 2782-1-130A (BSI, 1991b) using a Grant BT5D heating block. Samples were cut from the prepared milled hides and extrusion strips as described in section 4.1. Ten 5 mm x 5 mm sample were cut and placed in a test, a 50 mm piece of Congo red indicator paper was placed on the edge with 40 mm inside the tube and 10 mm outside the test tube. Samples were then placed into the heating block at 200°C. The insertion time was recorded. The samples were removed when the Congo red indicator paper started to turn from red to blue. The removal time was recorded. The Congo red time was calculated from the difference between the insertion time and the removal time. Ten tests were completed for each sample produced.

4.2.5 Tensile Properties

Samples for tensile testing were prepared using a 150 mm x 150 mm x 2 mm mould and were compression moulded using a Neoplast HYD 30T hydraulic press. A dumbbell shaped

cutting tool as described in BS 2782-3-320A-320F (BSI, 1976a), was used cut 5 samples from the prepared plaque. The testing was completed for each phase as follows.

4.2.5.1 Phase 1

The tensile properties were tested using a variation of BS 2782-3-320A-320F (BSI, 1976a) on a Lloyd Instrument LRX tensile tester (2.5 kN load cell) with the thickness being tested using a Wallace thickness gauge. Due to the limitations with this instrument the extension was measured by the instrument as the distance between the grips rather than the test area of the sample. Due to the limitations with the Lloyd Instrument LRX tensile tester an alternative instrument was sourced for all remaining phases.

4.2.5.2 Phase 2, Phase 3, and Phase 4

The tensile properties were tested using a Tinius Olsen H10KS/06. A variation of BS 2782-3-320A-320F (BSI, 1976a), in which the speed was reduced to 100 mm/min to more easily determine when the test pieces were breaking and whether it was within the test area. The parameters used can be found in Table 4-5.

Table 4-5: Test parameters used on the Tinius Olsen H10KS/06 tensile tester.

Tensile Parameters	
Load Range	1000 N
Extension Range	1000 %
Speed	100 mm/min
Preload	0.5 N

4.3 Spectroscopic Testing

Samples for spectroscopic analysis were prepared using a 150 mm x 150 mm x 2 mm mould and were compression moulded using a Neoplast HYD 30T hydraulic press. The spectroscopic techniques used in the study are outlined below.

4.3.1 Raman Spectroscopy

Raman spectroscopy was used in conjunction with the ATR-TIR as an alternative molecular vibrational technique to determine the chemical composition of the pPVC. All Raman

spectroscopic testing was completed using a Scientific DXR Raman Microscope; Table 4-6 outlines the settings used. Ten spots were tested on each sample. Smart background was used, which accounts for the background effects of the environment. Samples were secured to a glass slide and wipes with ethanol to remove any surface contaminants.

Table 4-6: DXR Raman microscope parameters used for measurements performed on a 25 mm x 25 mm sample of each formulation.

Raman Parameters	
Laser	532 nm
Power	10 mW
Grating	900 lines/mm
Spectrograph Aperture	25 µm pinhole
Microscope Objective	x 10
Exposure Time	5.00 sec
Number of Exposures	50
Number of Background Exposures	512
Photo Bleaching Time	0.5 min

4.3.2 FT-IR Spectroscopy

IR analysis is a vibrational spectroscopic technique providing qualitative and semi-quant data on the functional groups/molecules present in the sample. It was completed to collect spectroscopic data on all samples for spectral analysis. Spot tests were conducted on a Thermo Scientific Nicolet iS5 FT-IR Spectroscope;

Table 4-7 outlines the settings used for the test. ATR-Correction was used on all samples as standard; ten spots were tested on each sample. Background collections were completed every 10 tests, with the test surface being cleaned before and after every test.

Table 4-7: Nicolet iS5 FT-IR parameters used to perform measurements on samples of each formulation.

FT-IR Parameters	
Accessory	ID5 ATR Diamond
Sample Scans	32
Collection Time	25.6 Sec

4.3.3 Spectroscopic Analysis

4.3.3.1 WIRE

WIRE 2.0 (Renishaw) was used to perform the deconvolution on both the Raman and FT-IR spectroscopic data. Peak positions were manually selected and used to provide optimal

deconvolution parameters. A combination of Gaussian and Lorentzian peak shapes was used with a maximum of 3000 iterations, and a tolerance of 0.001. The peaks used have been outlined for each instrument and raw material in Section 5.

4.3.3.2 Origin

The Peak Analyzer function on Origin (Origin Lab Corporation) was used to perform deconvolutions on both the Raman and FT-IR spectroscopic data. Peak positions were first detected by the software and then manually adjusted to ensure all major peaks had been identified. The peaks used have been outlined for each raw material in Section 5.

4.3.3.3 Custom Software

Two custom software packages were created to fit FT-IR and Raman spectroscopic data.

4.3.3.3.1 FT-IR Spectroscopy – FTIR-fitting

FTIR-fitting is a curve matching script for FT-IR spectra of PVC, based on PVC resin, DOTP plasticiser, calcium carbonate filler and a calcium-zinc stabiliser package.

FTIR-fitting can be found at <https://github.com/robertsparkes/ftir-fitting-pvc>

The peaks used have been outlined for each instrument and raw material in Section 5.

4.3.3.3.2 Raman Spectroscopy – Raman-fitting

Raman-fitting is an automated peak fitting script for Raman spectra based on PVC resin, DOTP plasticiser, calcium carbonate filler and a calcium-zinc stabiliser package. (Sparkes et al., 2013; Sparkes, 2013).

Raman-fitting can be found at <https://github.com/robertsparkes/raman-fitting-pvc>

The peaks used have been outlined for each instrument and raw material in Section 5.

The next chapter, Chapter 5, compares the accuracy and suitability of the three different methods of spectral deconvolution for the chosen peaks of interest investigated,

5. Results and Discussion – Spectral Analysis

Accurate peak fitting of spectroscopic data is of crucial importance, for both qualitative and quantitative analysis. Software packages, usually part of the instrument's operating system, are often limited to finding the best fit using generalised parameters. For complex systems, such as, polymer materials composed of a combination of different crystalline and amorphous phases, peak fitting using instrument software can provide erroneous results. In the context of this work, wherein peak fitting forms the basis of data to be inputted into a model, a robust, cost-effective, repeatable, and fast method of achieving this is required. Whilst there are several software packages that can be used to complete peak fitting (including deconvolution if required) of spectroscopic data, these come with a price tag attached, thereby limiting industrial use. For the model proposed in this chapter to be adopted by the PVC industry, it needs to be based on an affordable, accurate, automated, and fast routine capable of peak fitting and peak deconvolution. This chapter will look at a comparison between three approaches to achieve this objective: Origin, WiRE 2.0, and an automated peak fitting script "Raman-fitting" using open-source software for Raman spectra, and a curve matching script "FTIR-fitting" for FT-IR spectra.

To determine the best option out of the software described the spectroscopic data collected from the Phase 1 samples was used. For each software, the data of interest for each raw material was normalised, to percentage, to allow direct comparisons between the three different techniques. In the following subsections, the normalised spectroscopic data is compared with the raw material concentration for each raw material (K70 resin, DOTP plasticiser, GCC filler and calcium/zinc stabiliser package). This comparison was made to identify the correlation between the two values, determining how easily the spectroscopic data could be used to determine the raw material concentration.

5.1 FT-IR Spectroscopy

FT-IR spectroscopy was completed to determine whether it could be used to predict the raw material concentrations of PVC compound. To do this it was first required that the best options for spectral analysis were considered. Therefore, the Phase 1 data was compared to the deconvolution and curve fitting data from Origin, WiRE, and the FTIR-fitting software. Numerous facts were considered for the comparisons, such as ease of use and the time required. The decision was dependant on the strength of the correlation found between the FT-IR peak response and the raw material concentrations. Figure 2-1 gives an example FT-IR spectrum for a typical PVC compound formulation.

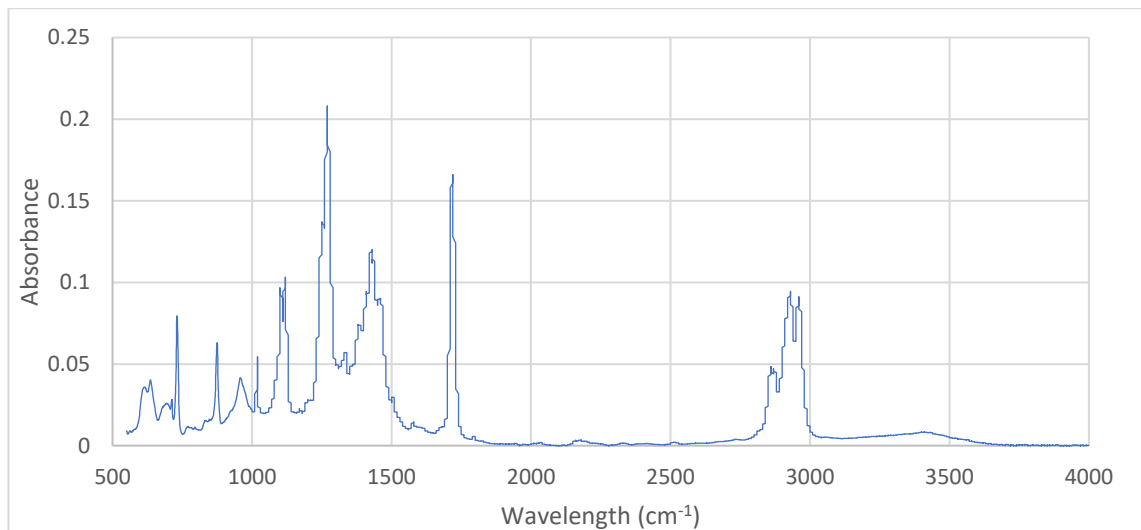


Figure 5-1: Example FT-IR spectrum for a typical PVC compound formulation.

5.1.1 PVC Resin

For PVC, the peak at 635 cm^{-1} was used for WiRE 2.0 and Origin, this is a result of the C-Cl stretching in the PVC. FTIR.fitting used the peak heights from multiple fitted peaks to provide a peak response based on the spectra for PVC resin.

The correlation between the normalised spectral data from each piece of software and the PVC concentration (in percentage) is shown in Figure 5-2. For all three pieces of software a variation was found across the data. A similar pattern in the data can be found with FTIR-fitting and Origin. Origin shows a higher range than FTIR-fitting at each PVC resin

concentration below 70%, whereas above 70% the range in the FTIR-fitting is higher. Both Origin and FTIR-fitting, show a correlation, demonstrated by R^2 values of 0.6031 and 0.7504. When using WiRE, a distinct group of datapoints can be seen outside of the main data, between 77.54 and 90.57 on the y-axis. Below 10 on the y-axis, between 30 – 45% PVC resin a series of 5 data points away from the main group creating further variance. Whilst the remaining data shows a similar pattern to the two software packages the groups described make it easy to understand why a low R^2 value of 0.4009 was achieved.

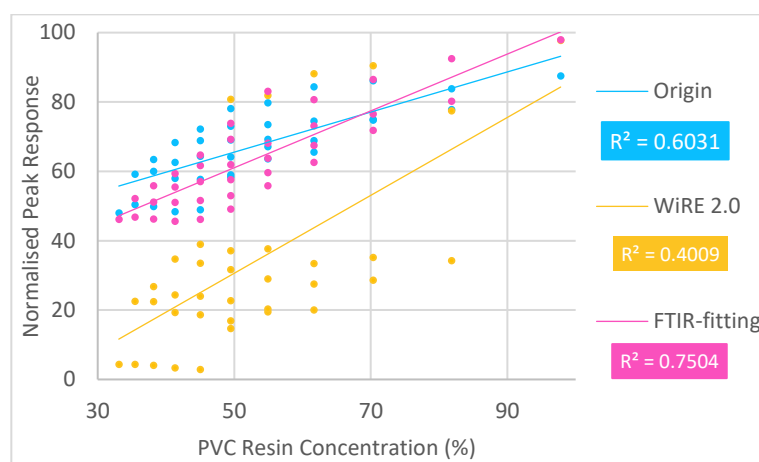


Figure 5-2: Graph giving the peak responses from the deconvolution of the Phase 1 FT-IR spectra, using the three different software packages over the PVC resin concentration.

5.1.2 DOTP Plasticiser

For DOTP plasticiser the peak 1019 cm^{-1} was used for WiRE 2.0 and Origin, this is aromatic C-H in-plane bending (Coates, 2006). FTIR-fitting used the peak heights from multiple fitted peaks to provide a peak response.

Plotting the peak response vs concentration percentage for DOTP plasticiser gives a strong co-variance (Figure 5-3). Testing via linear correlation gave R^2 values of 0.9625 for Origin and 0.9954 for FTIR-fitting. Linear correlation was weaker for WiRE 2.0, with an R^2 value of 0.6992 even when an outlier was removed. There is particularly high variation in peak response level with Wire 2.0 for DOTP concentrations between 15 and 35%.

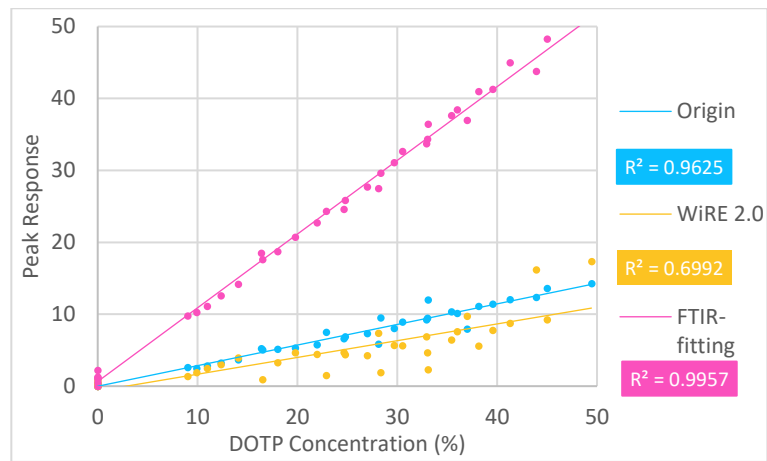


Figure 5-3: Graph giving the peak responses from the deconvolution of the Phase 1 FT-IR spectra, using the three different software packages over the DOTP concentration.

5.1.3 Calcium Carbonate Filler

For calcium carbonate filler the peak 1426 cm^{-1} was used for WiRE 2.0 and Origin, this is the ν_3 asymmetric CO_3 stretching from the carbonate ion (Gunasekaran et al., 2006).

FTIR.fitting used the peak heights from multiple fitted peaks to provide a peak response.

All three software packages gave high correlations when investigating the calcium carbonate filler (Figure 5-4). Origin and FTIR-fitting gave R^2 values of 0.9262 and 0.9295, respectively whereas, WiRE 2.0 gave an R^2 value of 0.8178. Showing a strong correlation between the calcium carbonate concentration and the normalised peak data.

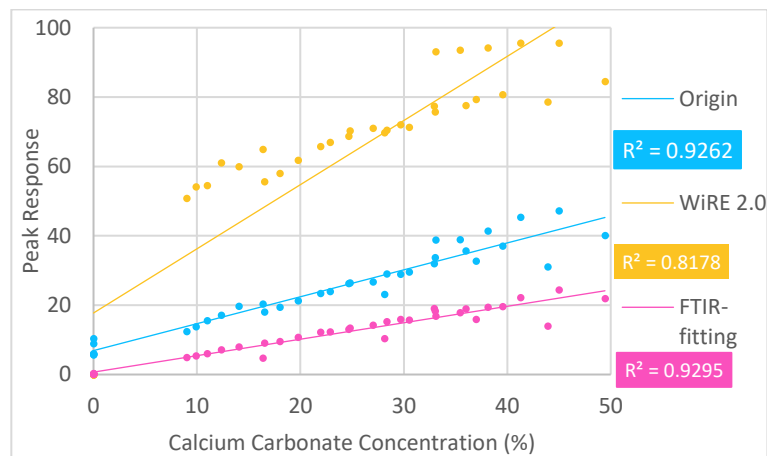


Figure 5-4: Graph giving the peak responses from the deconvolution of the Phase 1 FT-IR spectra, using the three different software packages over the calcium carbonate concentration.

5.1.4 Stabiliser Package

For FTIR-fitting the stabiliser package was included in the curve fitting and therefore a peak response was obtained, however when using WiRE and Origin none of the peaks gave strong enough responses to successfully identify the presence of the stabiliser package. In this case the stabiliser package concentration was calculated from the PVC resin as a ratio of 100:2.25 (PVC: stabiliser package). It can be seen in Figure 5-5 that the result from FTIR-fitting when very varied, with an R^2 value of only 0.3593 being found.

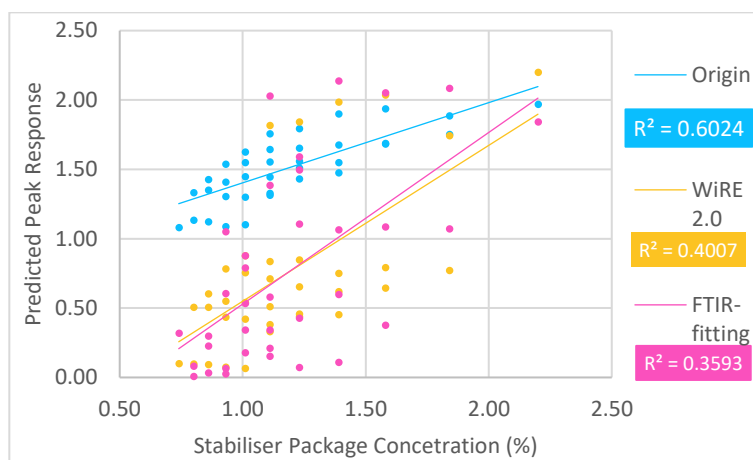


Figure 5-5: Graph giving the predicted peak responses for the stabiliser package (based on the PVC resin peak responses from the deconvolution of the Phase 1 FT-IR spectra) over the stabiliser package concentration.

5.1.5 FT-IR Spectroscopy Conclusion

From the data presented above it can be observed that Origin and the FTIR-fitting software are more well suited to the deconvolution of this FT-IR spectroscopic data. Whilst WiRE 2.0 did show correlations, these were mostly very weak and would not be well suited to the creation of a predictive model. When considering both the correlations found, and the advantages and disadvantages of each piece of software, the FTIR-fitting software would be the most appealing due to being free source software and the fastest to achieve results, which would appeal to the PVC industry.

5.2 Raman Spectroscopy

Raman spectroscopy was completed to determine whether it could be used to predict the raw material concentrations of PVC compound. To do this it was required that the best options for spectral analysis were considered. Therefore, the Phase 1 data was compared to the deconvolution and curve fitting data from Origin, WiRE, and the FTIR-fitting software. Numerous facts were considered for the comparisons, such as ease of use and the time required. However, the decision was mostly dependant on the strength of the correlation found between the Raman peak response and the raw material concentrations.

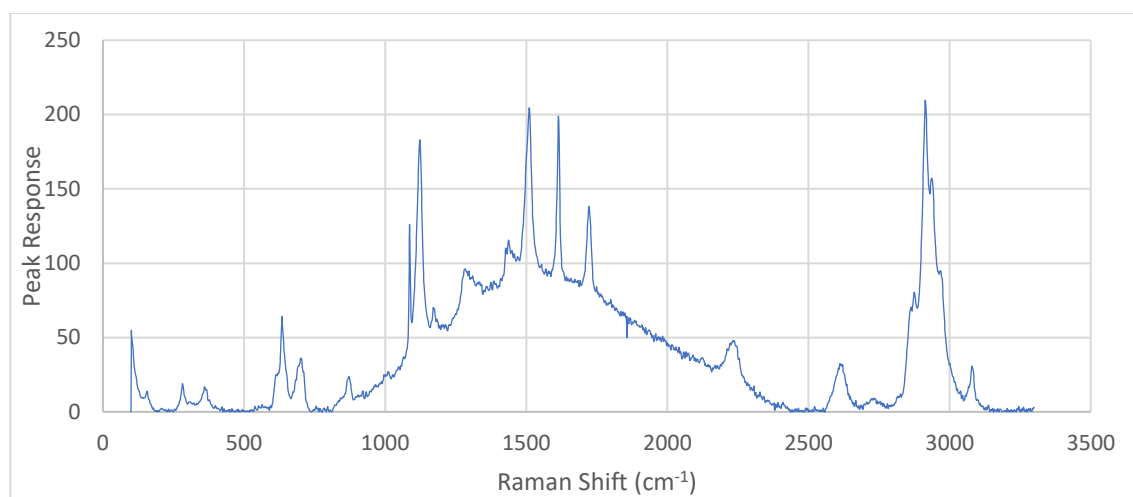


Figure 5-6: Example Raman spectrum for a typical PVC compound formulation.

5.2.1 PVC Resin

For both WiRE 2.0 and Origin the peak at 639 cm^{-1} was chosen for quantification, this is a result of C-Cl stretching within the polymer (Klisinska-Kopacz et al., 2019). Raman fitting used the peak heights from multiple fitted peaks to provide a peak response.

Raman fitting showed a relatively strong correlation, with the lowest variance seen in the data points out of the three programs (Figure 5-7). This correlation was reflected by an R^2 value of 0.7415. The results found from WiRE showed a correlation was present, however the data was over a smaller range overall, this correlation was seen with an R^2 value of 0.6064. The variance seen with Origin was much greater, especially from 45 – 70%, this was reflected in the R^2 value being 0.5062.

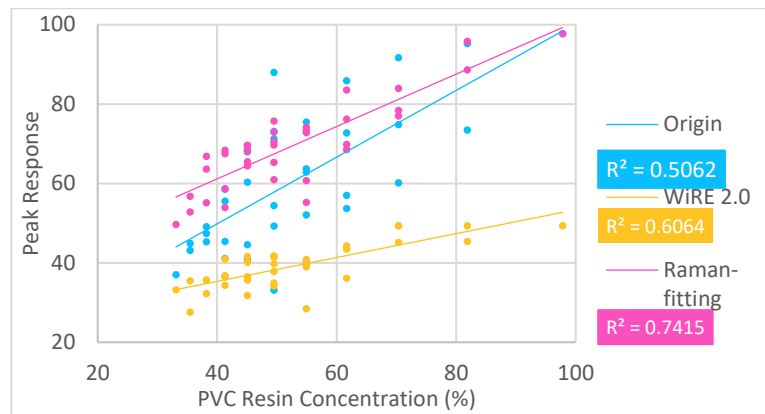


Figure 5-7: Graph giving the peak responses from the deconvolution of the Phase 1 Raman spectra, using the three different software packages over the PVC resin concentration.

5.2.2 DOTP Plasticiser

For DOTP the peak 1615 cm^{-1} was used for WiRE 2.0 and Origin, this is in the C-C stretch.

Raman spectroscopy the peak at 1615 cm^{-1} (in the aryl C-C stretch) (Socrates, 2001).

Raman.fitting used the peak heights from multiple fitted peaks to provide a peak response.

When looking at the DOTP concentration versus the peak response, as found in Figure 5-8,

the strong correlation is found from Origin giving a high R-squared value of 0.9439. Higher

variance can be seen when using WiRE 2.0 and the Raman-fitting. When using WiRE there

are 7 datapoints that fall directly on the x-axis, with no peak being found, despite these

points, the correlation in the data can still be seen, with an R² value of 0.7307 being found.

A general trend can be seen in the data when using Raman-fitting, however the variance

can be seen in the data, the variance is greatest between 20 – 40% DOTP, the R² value

found is 0.7247.

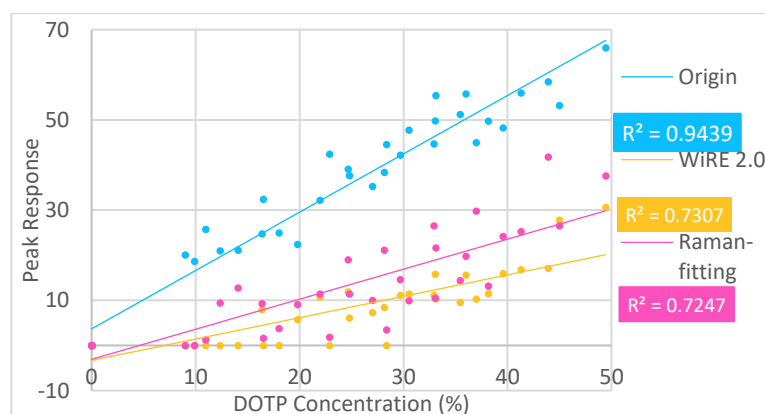


Figure 5-8: Graph giving the peak responses from the deconvolution of the Phase 1 Raman spectra, using the three different software packages over the DOTP concentration.

5.2.3 Calcium Carbonate Filler

For DOTP the peak 1088 cm^{-1} was used for WiRE 2.0 and Origin, caused by multiple C-O stretches within the calcium carbonate (Gunasekaran et al., 2006). Raman fitting used the peak heights from multiple fitted peaks to provide a peak response.

A positive correlation can be seen between the calcium carbonate concentration and the peak response, however significant variance can be seen (Figure 5-9), between 20 – 40% all three programs show significant variance in the datapoints. Raman-fitting shows the strongest correlations, however there are a collection of points between a peak response of 30 – 40 that do not lie with the main trend of the data. In addition, several points can be seen that drop below the overall trend. Despite this the correlation is still relatively strong, with an R^2 value of 0.7407 being found. The correlation found for Origin looks strong however the presence of datapoints such the one at $x = 43.90$, $y = 22.78$, have lowered the correlation, resulting in an R^2 value of 0.6487. A poor correlation between the calcium carbonate concentration and peak response found when using WiRE 2.0, with 9 datapoints having no peak response, this is confirmed by R^2 value being 0.3496.

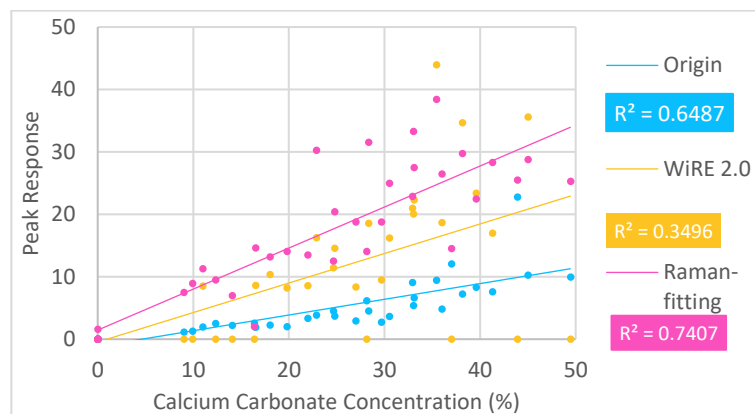


Figure 5-9: Graph giving the peak responses from the deconvolution of the Phase 1 Raman spectra, using the three different software packages over the calcium carbonate concentration.

5.2.4 Stabiliser Package

When using Raman spectroscopy, no reliable stabiliser peak could be identified, therefore, to account for the stabiliser package present a predicted concentration was calculated from

the PVC resin at a ratio of 100:2.25 (PVC resin: stabiliser package). Therefore, the correlations for the stabiliser package followed the pattern found for the PVC resin.

The correlation between the stabiliser package concentration alongside the calculated stabiliser peak response from the PVC resin peak response can be seen in Figure 5-10. The highest correlation was with the Raman-fitting software, which gave an R^2 value of 0.7419, followed by WiRE 2.0 and Origin, giving R^2 values of 0.5539 and 0.5062, respectively.

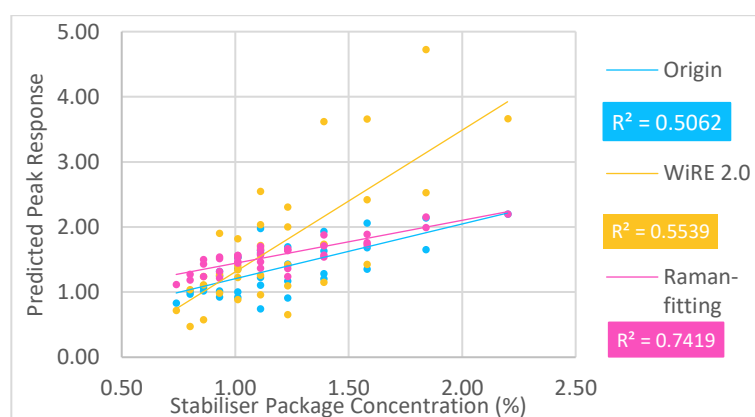


Figure 5-10: Graph giving the predicted peak responses for the stabiliser package (based on the PVC resin peak responses from the deconvolution of the Phase 1 Raman spectra) over the stabiliser package concentration.

5.2.5 Raman Spectroscopy Conclusion

When using Raman spectroscopy, when considering all four raw materials overall, Raman-fitting gave the best correlations. R^2 values were found of 0.7415 (PVC Resin), 0.7247 (DOTP), 0.7407 (Calcium Carbonate) and 0.7419 (Stabiliser Package). The other software gave far more variation, Origin gave a very strong correlation for DOTP, with an R^2 value of 0.9439, the remaining R^2 values all fell below 0.65. WiRE performed the worst, with its highest correlation giving an R^2 value of 0.7307.

Whilst correlations were found when using Raman spectroscopy, these offered a lower R^2 value than those observed using FT-IR. The weaker correlation in the Raman data would, if used, lead to less accurate predictions of PVC compound properties when compared to FT-IR. Ideally an R^2 value of greater than 0.8 would be required for both the DOTP and

calcium carbonate for this to be viable. With further work on both the collection method and the Raman-fitting, it is likely that this could be achieved in the future.

5.3 Conclusions

FT-IR has shown great potential when being used for predicting the raw material concentration from the peak data provided, when compared to the results found for Raman spectroscopy. In addition to FT-IR spectroscopy providing better correlations, it also has the advantage that it is more commonly used within the PVC industry. Therefore, for the creation of the model, FT-IR spectroscopy will be used as the primary technique. However, Raman spectral data was still collected for all samples produced, for use in further work.

Based on the software packages used in this study, Origin and the FTIR-fitting software provided good correlations for FT-IR. Both would require some initial training in their use, with Origin being initially easier to set up as the FTIR-fitting would likely have to be optimised for each company for which it is used. However, following this initially steep learning curve, once set up, FTIR-fitting would be the faster and easier to use option. The biggest key difference here is also that the FTIR-fitting software is open source, free to use, making it more attractive to the PVC industry. The FTIR-fitting software will be used to analyse FT-IR spectra data and the use of other pieces of software will be discounted.

The next chapter, Chapter 6, provides the property and spectroscopic results obtained for phases 1 – 3.

6. Results and Discussion – Phases 1 – 3

Chapter 5 showed that custom scripts for fitting FT-IR and Raman data are the best way to differentiate the amount of each ingredient in a PVC formulation. In this chapter, a databank of FT-IR data from known formulations will be generated. This is for the creation of a model that predicts the proportion of each ingredient in an unknown PVC formulation to be produced., called “Part 1” in chapter 7.

The final model will also predict the material properties from the raw material concentrations, called “Part 2” of the model in chapter 7. A databank is required to form the backbone of the predictive model as well as a training set to test the model against.

Three phases of work were completed across a range of different raw material addition rates to build up the databank. The variables used are discussed in the following sections with all 96 formulations being outlined in Section 4.1.

6.1 Phase 1 & Phase 2 Variables

Phase 1 consists of 36 individual formulations based upon K70 resin, DOTP plasticiser GCC filler and a calcium-zinc stabiliser package, all prepared on a two-roll mill. Phase 2 consists of 25 further formulations based on the same four raw materials, prepared using a 2-stage mixer. Therefore, between these two phases the only difference was the compounding method and the concentration levels of the raw materials.

6.2 Phase 3 Variables

Phase 3 consisted of 35 individual formulations where the type of raw materials was varied, to determine the potential obstacles the predictive model could face. For each test in Phase 3, these are divided into the following subsections:

Resin Variations – Exploring the test results when using different K-value resins, K66, K70, K80, K100.

Plasticiser Variations – Exploring the use of DINP as an alternative to DOTP plasticiser, as well as studying the use of ESBO as a secondary plasticiser within PVC compound.

Filler Variations – Considering the use of higher-grade calcium carbonate fillers, with a smaller particle size, stearic coatings, and precipitated fillers.

Stabiliser Pack Variations – Exploring the impact of changing the stabiliser package addition rate within PVC compound.

6.3 Industrial Testing

In the PVC industry there are certain tests that are completed as standard and quoted to customers on technical datasheets, as well as being included in some QC specifications. Therefore, it is important that these tests are predicted so that minimal testing is required, giving the model true value and industrial relevance. Therefore, BSS, Shore A, relative density, Congo red heat stability, and tensile testing (focusing on the tensile strength and elongation at yield) were all completed to give an overview of the material properties of each sample. The results of the physical property testing will now be discussed.

6.3.1 British Standard Softness

The following section explores the relationship between the BSS and the different raw materials. Initially it looks at the data collected within phases 1 and 2, investigating only four raw materials (K70 resin, DOTP, GCC and a calcium-zinc stabiliser package), followed by the impact of variation of raw materials used within phase 3 on BSS.

6.3.1.1 Phase 1 & 2

The effect of PVC formulation changes on softness was investigated by plotting BSS results against raw material concentration % (Figure 6-1).

Variations were observed between BSS and concentration for each raw material, the strongest relationship was between BSS and DOTP plasticiser. The BSS increases as the concentration of DOTP plasticiser increases. A quadratic correlation test gave an R^2 value

of 0.9134 for this relationship. This correlation is to be expected, as the key purpose of plasticiser is to lower the glass transition temperature of a material to increase its flexibility. All other raw materials showed a negative correlation with BSS as their respective concentrations were increased. Weak negative correlations ($R^2 = 0.18 - 0.32$) with other raw material concentrations are due to co-variance in DOTP concentration: increasing other raw materials reduces DOTP concentration and therefore decreases softness. The relationship between BSS and DOTP concentration was investigated further by separating the dataset based on the concentration of GCC in PHR (Figure 6-2). When the GCC filler concentration is considered alongside the DOTP plasticiser concentration, GCC was shown to have an influence: as the concentration of GCC increases, softness decreases. As can be seen in Figure 6-2 the samples that do not contain GCC, are situated the furthest from the bulk of the data and have the lowest R^2 value of 0.9769. Those that contain GCC, all had R^2 values of greater than 0.9974, showing strong correlations.

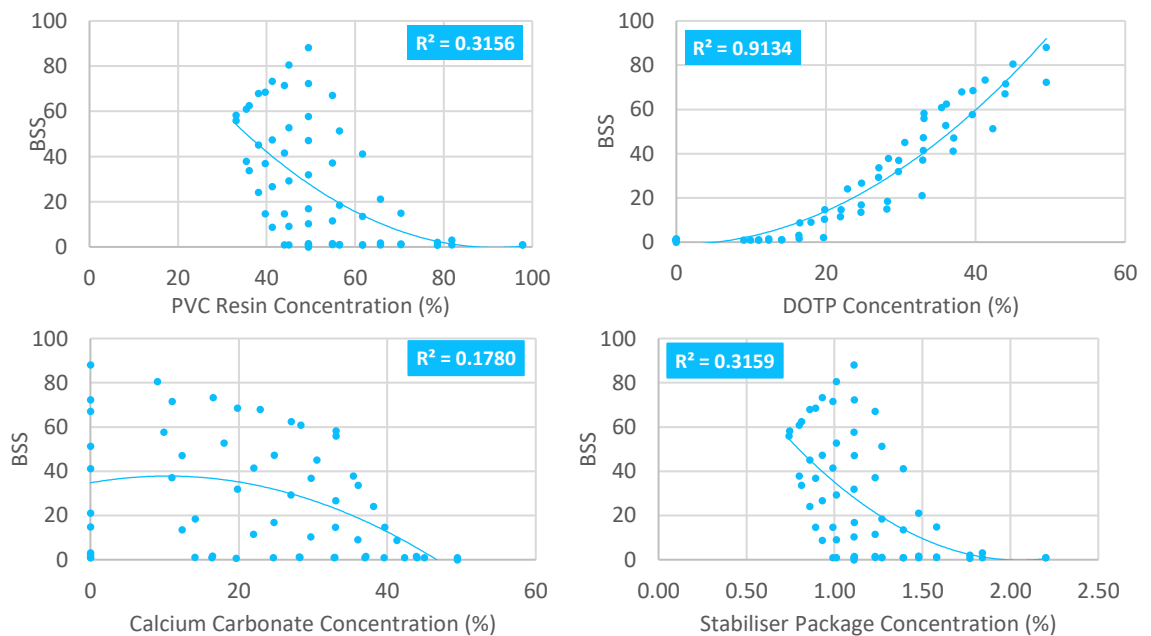


Figure 6-1: Graphs of the concentration of each raw material used within Phase 1 and Phase 2, are shown vs the average BSS of each sample.

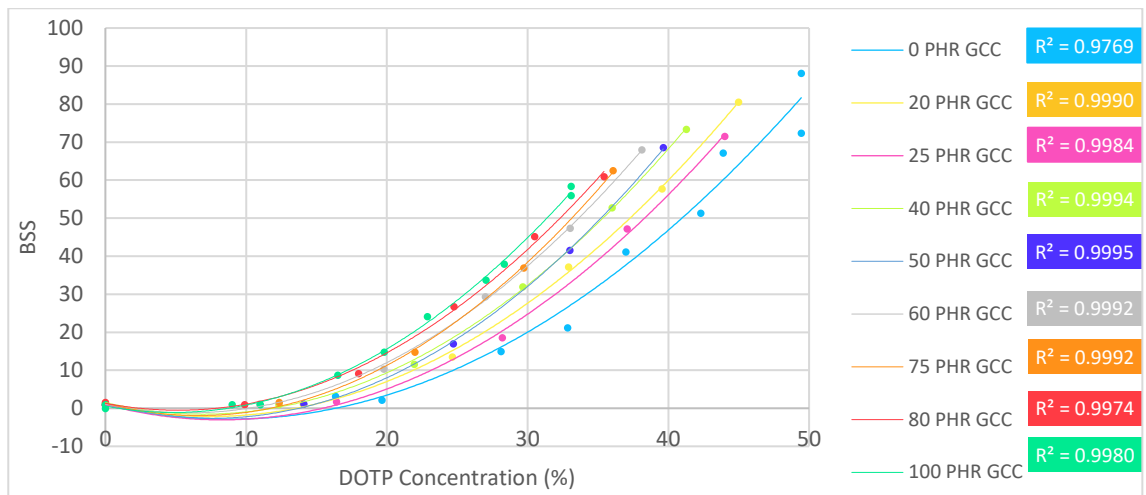


Figure 6-2: Graph showing the DOTP concentration, in percentage, vs the BSS, with the data categorised by the calcium carbonate concentration, in PHR.

6.3.1.2 Phase 3 – Raw Material Variations

In this section the BSS was compared with the different raw materials investigated in phase 3 to determine the relationships present and how they may affect a predictive model.

6.3.1.2.1 Resin Variations

PVC resin K-value refers to the difference in polymer chain length (see section 0 for more details). A difference of 3.8 in BSS between the lowest K-value, K66, and the highest K-value, K100 was observed, which at 50 PHR DOTP (as was used for these comparisons) is considered significant within the industry. However, the difference in softness between K70 and K100 is only 1.2, and that would be within specification when performing industrial QC testing. Plotting BSS vs. K-value gives a negative linear correlation with R² value of 0.6427 (Figure 6-3). A reduction in BSS with increasing K-value is to be expected, as the K-value increases the absorption of plasticiser by the PVC resin increases.

The relative importance of changing K-value and/or DOTP concentration was investigated by plotting BSS against DOTP concentration individually for K70 and K100 specimens (Figure 6-4). Although the correlation coefficients for both K70 and K100 are >0.9 and the trendline suggests that K70 gives slightly higher BSS, the K70 data is much more scattered and displays bimodal or non-linear behaviour. At lower DOTP concentrations the softness is

similar and below the regression line. At the higher end, more variation in softness is observed and most of the points lie above the line.

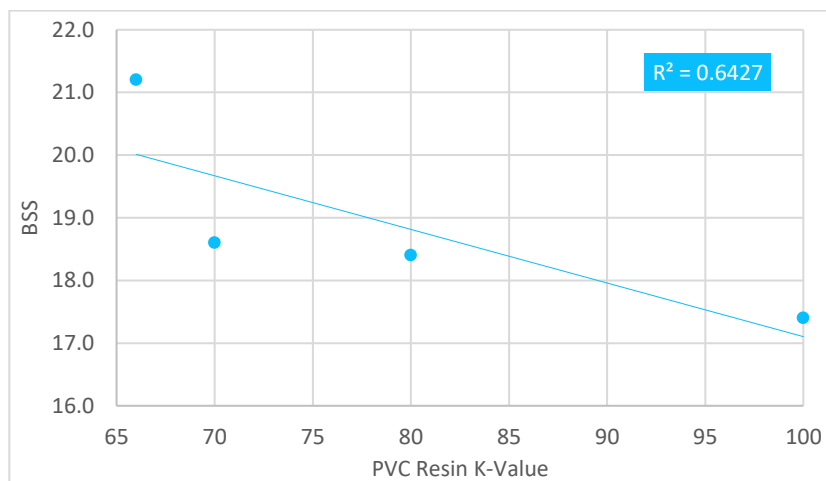


Figure 6-3: Graph of the BSS found when changing the PVC resin K-Value.

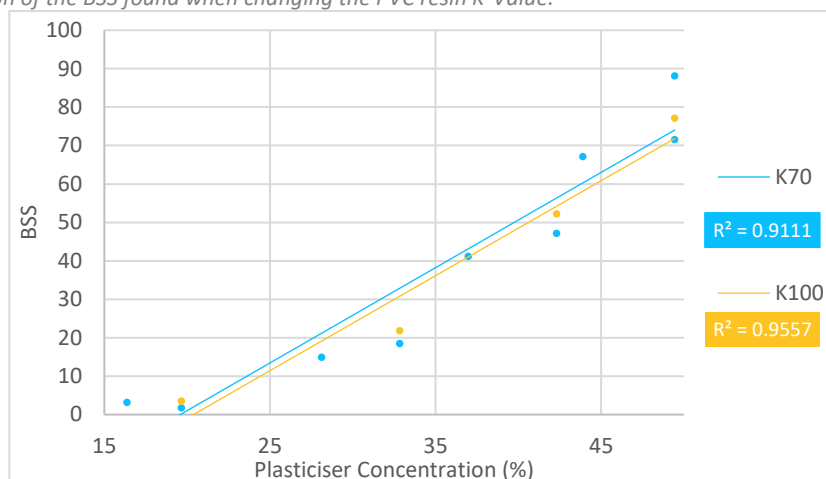


Figure 6-4: Graph showing the differences found in BSS between K70 and K100 PVC resin with increasing DOTP concentration, in percentage.

Based on this initial dataset, there is not a great enough difference between K-values to include this variable when modelling BSS.

6.3.1.2.2 Plasticiser Variations

Two different plasticisers were investigated as outlined below.

6.3.1.2.2.1 DINP

DINP is a plasticiser commonly used for GP PVC compound (this is discussed in section 0. A comparison BSS versus the plasticiser concentration in percentage is shown in Figure 6-5. It was found that the BSS increased with increasing plasticiser concentration, for both DOTP and DINP. As can be seen, the data gives very similar BSS results, with an some datapoints

very close to each other. This relationship is expected as the two plasticisers are sold as having a similar absorption efficiency within PVC compound.

For the purposes of a predictive model with regards to BSS, the primary plasticiser type will not be considered because the most used plasticisers in the UK, DOTP and DINP, gave results that were not significantly different. However, it is worth noting that other plasticisers, such as DOA and DPHP may give different results.

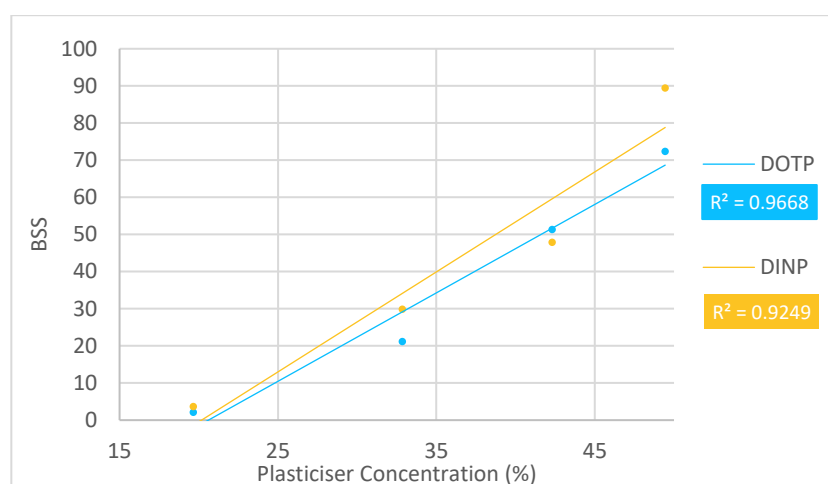


Figure 6-5: Graph showing the plasticiser concentration in percentage versus the BSS, for DOTP and DINP plasticiser.

6.3.1.2.2.2 ESBO

ESBO is a plasticiser that is added to pPVC in small quantities (5 - 10 PHR) to save costs and provide additional properties, such as heat stability. BSS variation was tested for DOTP with and without ESBO (5 PHR concentration). There was no significant difference seen with and without ESBO (Figure 6-6), and therefore ESBO, as a secondary plasticiser, will not be considered when producing a predictive model of PVC.

Whilst ESBO is generally only used as a secondary plasticiser, with the current concern surrounding the environment there is an increasing level of interest in using ESBO and similar plasticisers at higher loading. Therefore Figure 6-7 shows the effect of an increasing ESBO concentration within a formulation containing 50 PHR total plasticiser (therefore as the ESBO increases the DOTP decreases). Overall, there is a downwards trend with increasing ESBO, when the point with 0% ESBO is removed. The greatest difference in BSS

is 2.4, therefore further investigation would be required to determine the level of significance here and how it would impact the model.

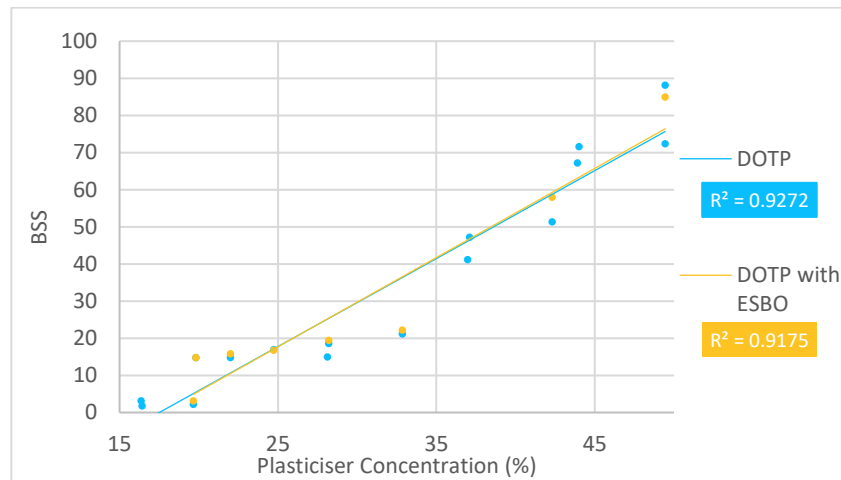


Figure 6-6: Graph showing the plasticiser concentration in percentage versus the BSS, for DOTP plasticiser and DOTP plasticiser with 5 PHR being replaced with ESBO plasticiser.

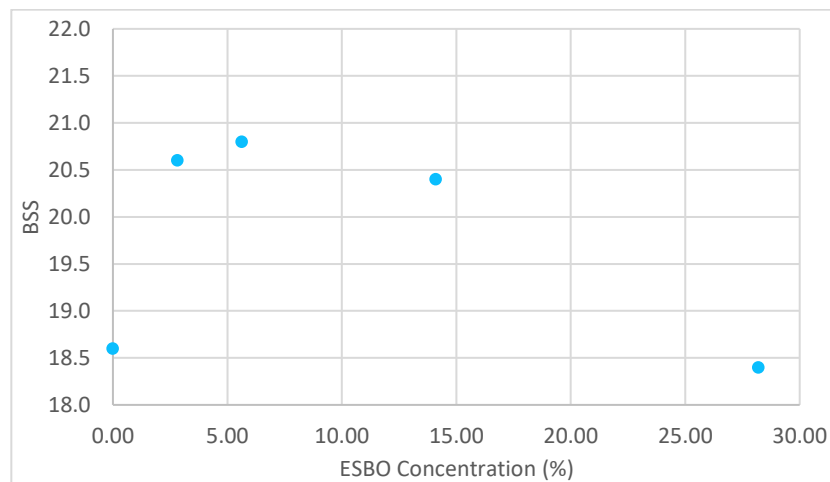


Figure 6-7: Graph showing how the BSS changes with an increase in the ESBO concentration (as a replacement for the DOTP in a 1:1 ratio) in PVC compound.

6.3.1.2.3 Filler Variations

When using filler in pPVC there are several options available, as discussed in section 2.3.5.1, therefore it was important to investigate the types of calcium carbonate filler available.

Figure 6-8 gives the BSS for the four different calcium carbonate fillers used: GCC, fine GCC, coated GCC and PCC. The largest difference is seen between the GCC and the other fillers. These fillers have smaller particle sizes and additional treatments, such as coating and/or precipitation, this difference could be a direct result of these changes. It is worth noting that the differences found in the BSS are all less than 2.2, and therefore this difference is

close to the tolerances used within the PVC industry when completing QC testing.

Figure 6-9 shows the differences found in BSS for two of the calcium carbonate fillers, with the BSS being measured as the calcium carbonate concentration increases. The data shows that with this increase, the BSS of the PVC compound decreases with a difference of at least 2.4 BSS between the two types of calcium carbonate. The results found from Figure 6-8 and Figure 6-9 show that there is a difference between the calcium carbonate types. Due to the difference found, further investigation would be required to determine how significant this difference is before this could be confidently added to the model.

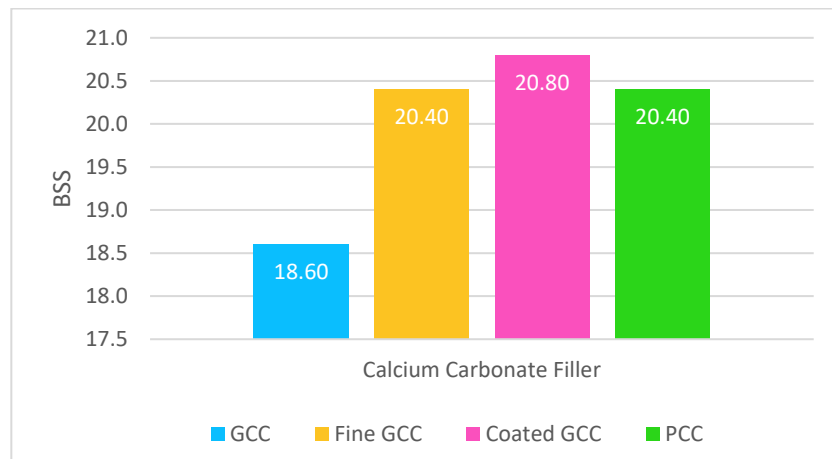


Figure 6-8: Chart showing the BSS when using different calcium carbonate fillers at the same concentration.

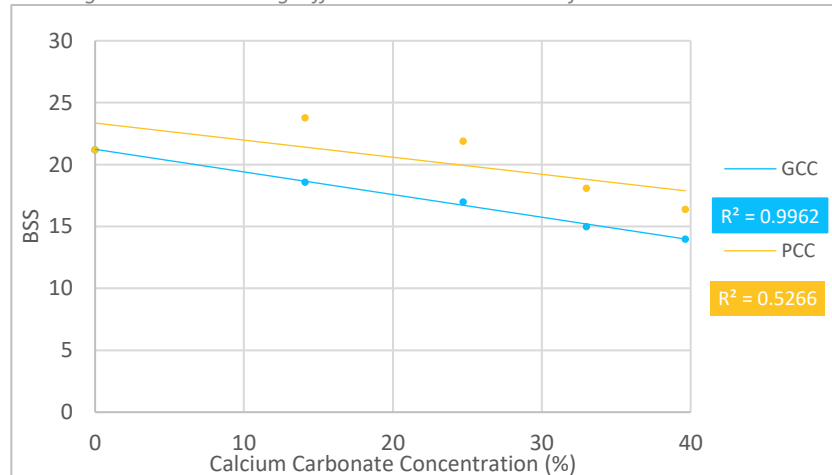


Figure 6-9: Graph showing the influence of two different calcium carbonates on the BSS with an increase in the concentration, in percentage.

6.3.1.2.4 Stabiliser Pack Variations

In GP pPVC the stabiliser package tends to be used at a loading of 2 – 2.5 PHR, which is why 2.25 PHR was selected for the phase 1 and 2. Different levels of stabiliser packages can be

used to boost stability or lowered to increase the clarity of an unfilled sample, therefore it was important to ensure that the stabiliser package level was investigated.

Figure 6-10 shows the influence of the stabiliser package concentration on the BSS. There is no significant influence from the stabiliser package concentration on the BSS, with the difference between the highest and lowest values being only 0.6. As expected due to the low addition rate. Industrial weighing error would be more likely to cause larger variations.

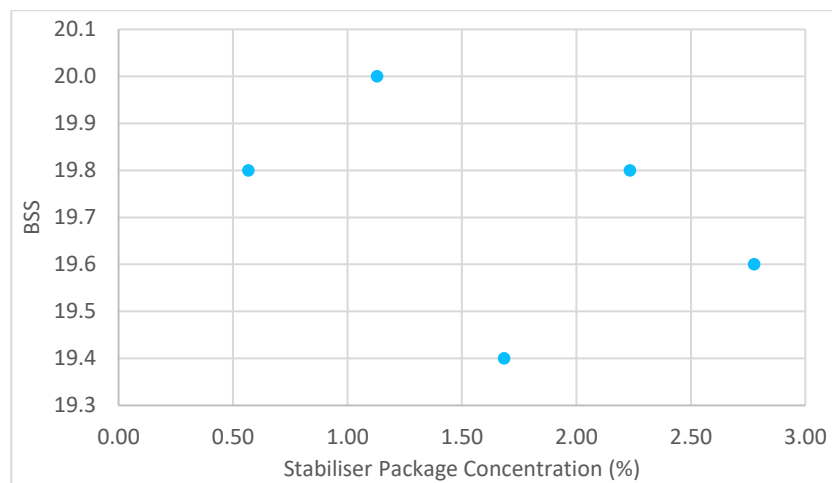


Figure 6-10: Graph showing the influence of the stabiliser pack concentration, in percentage, versus the BSS.

6.3.2 Shore A Hardness

BSS and Shore A hardness are both used as measures of the softness (or hardness) of a material, they were compared to see whether it is required for both to be tested. Figure 6-11 shows the graph of BSS versus Shore A hardness.

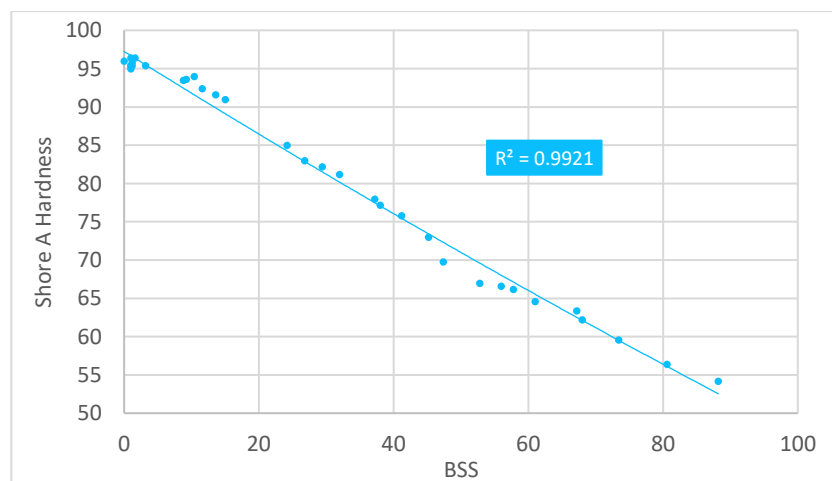


Figure 6-11: Graph showing the relationship between BSS and Shore A hardness, with a linear line of fit.

There is a clear correlation between the two tests, with the Shore A decreasing as the BSS increases. The R^2 value supports this observation with a value of 0.9921, showing a strong correlation. Going forwards BSS will be tested with Shore A hardness being calculated from the BSS when required.

6.3.3 Relative Density

The following section explores the relationship between the relative density and the different raw materials. Initially it looks at the data collected within phases 1 and 2, investigating at only four raw materials (K70 resin, DOTP, GCC and a calcium-zinc stabiliser package). It then will look at the more varied raw materials used within phase 3 and their relationship with relative density.

6.3.3.1 Phase 1 & 2

The percentage raw material versus relative density in Figure 6-12 shows the strongest correlation is found with calcium carbonate. An increase in the relative density as the concentration of calcium carbonate increases is observed, which is expected. This is due to the density of calcium carbonate being significantly higher than the density of other raw materials and so it has a larger impact at low addition rates.

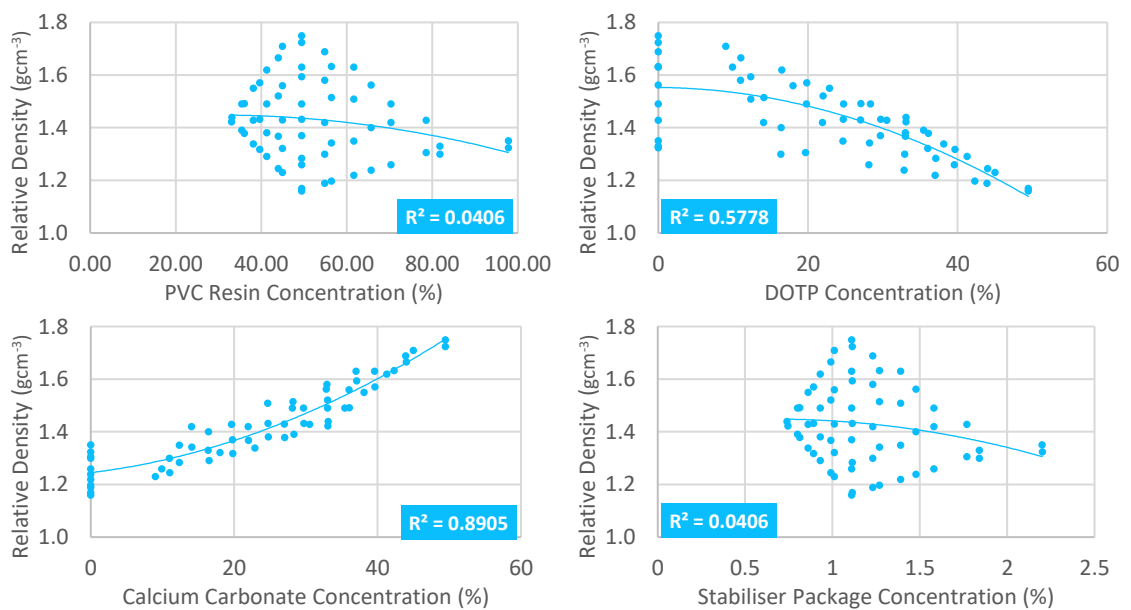


Figure 6-12: Graphs of the concentration of each raw material used within Phase 1 and Phase 2, shown vs the average relative density of each sample.

Figure 6-13 the data has been further divided by the DOTP concentration (in PHR). A correlation is found at each DOTP plasticiser concentration, as the plasticiser concentration increases the relative density decreases with the lowest R² value being 0.9898.

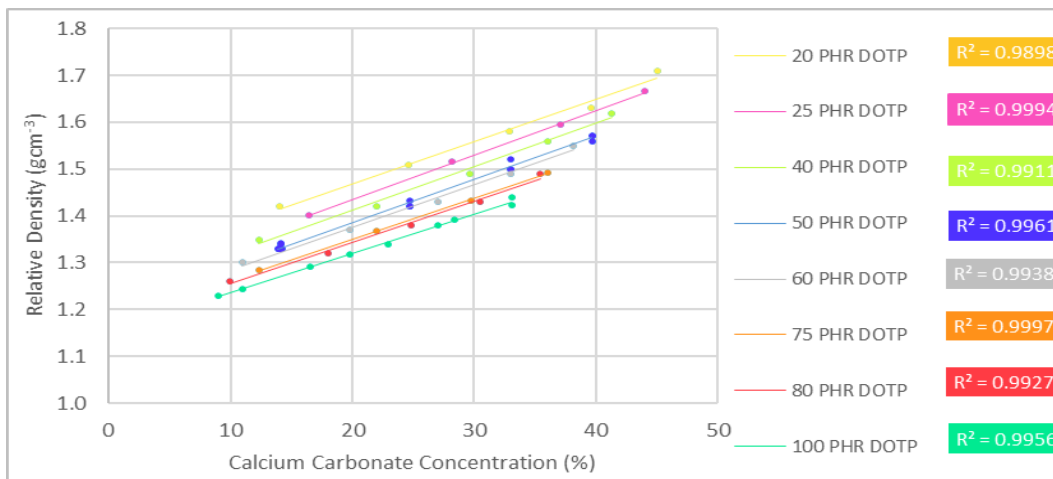


Figure 6-13: Graph showing the calcium carbonate concentration, in percentage, vs the relative density, with the data categorised by the DOTP concentration, in PHR.

The results found in this section shows a strong relationship between the relative density and the calcium carbonate, with DOTP providing further clarity. These correlations can thus be used in the predictive model.

6.3.3.2 Phase 3 – Raw material Variations

In this section the relative density was compared with the different raw materials investigated in phase 3 to determine the relationships present and how they may affect a predictive model.

6.3.3.2.1 Resin Variations

The relative density with changing K-value was investigated to determine whether there was any influence of the polymer chain length on the relative density, and whether this would need to be considered within a predictive model.

Figure 6-14 shows the influence of PVC resin K-value on the relative density of the PVC compound. All four resins gave, within experimental error, the same relative density demonstrating that changing the K-value of the resin results in no observable difference in the relative density of the PVC compound.

Figure 6-15 shows the impact on the relative density with plasticiser concentration for both K70 and K100 resins. As can be seen, the results for both resins are within the margin of error, both producing similar lines of fit with high correlations.

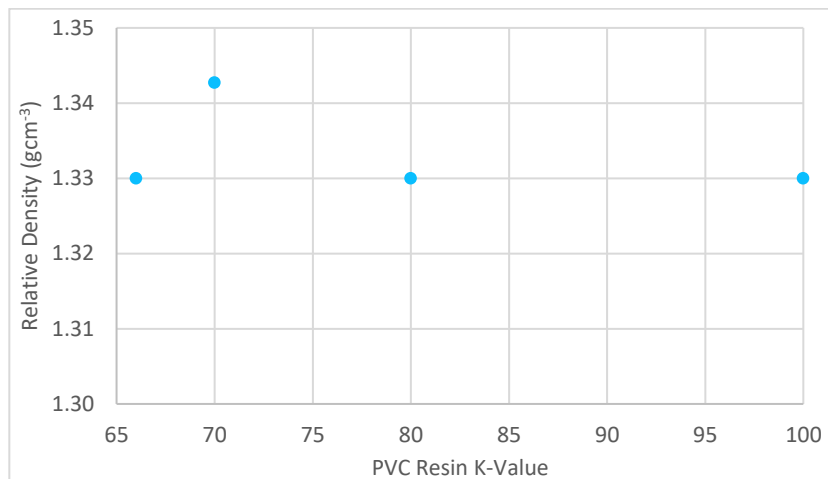


Figure 6-14: Graph of the relative density found when changing the PVC resin K-Value.

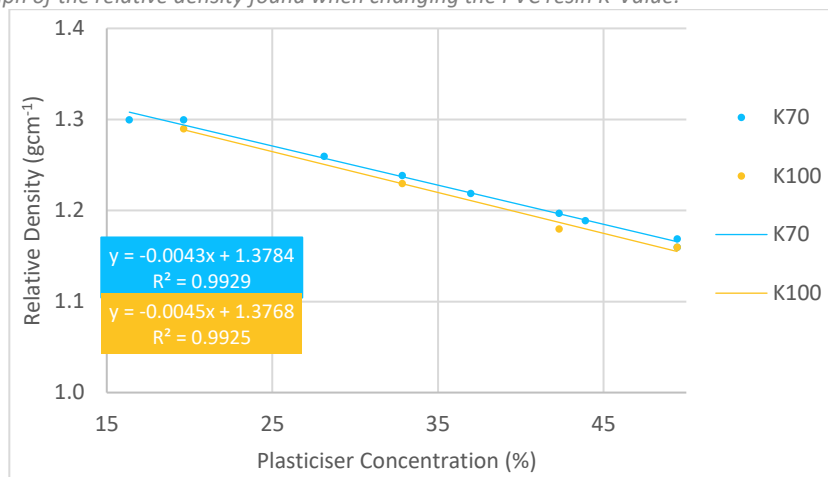


Figure 6-15: Graph showing the differences found in relative density between K70 and K100 PVC resin with increasing DOTP concentration, in percentage.

6.3.3.2.2 Plasticiser Variations

Different plasticisers have different relative densities; therefore, it is important to investigate how this can influence the relative density of a PVC compound.

6.3.3.2.2.1 DINP

The relationship between the relative density and the plasticiser concentration for both DOTP and DINP was investigated in Figure 6-16. The DINP samples gave lower relative density results, however the difference observed was only 0.02 gcm⁻³ and within the standard tolerances that would be found in an industrial QC setting. This is expected, as

the densities of DOTP and DINP are 0.984 gcm^{-3} and 0.980 gcm^{-3} , respectively. This demonstrates the plasticiser type (DOTP or DINP) does not need to be accounted for to predict the relative density of a PVC compound and that the density of the plasticiser itself could be used to determine if this should be considered in future iterations of the model.

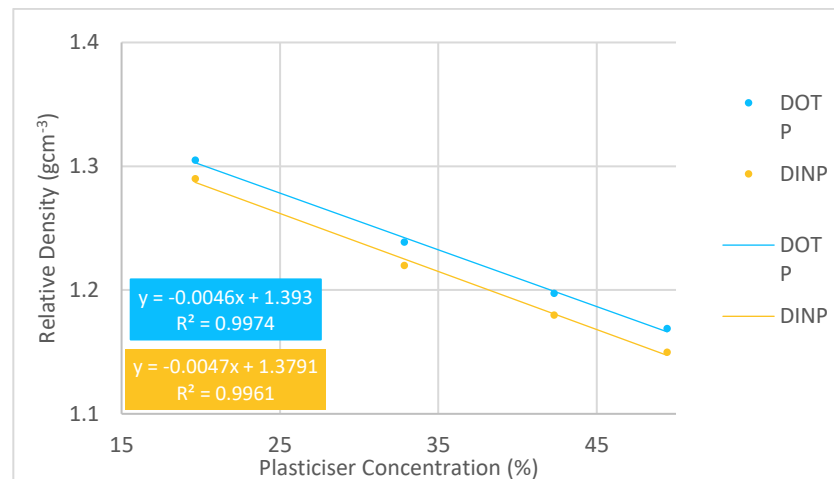


Figure 6-16: Graph showing the plasticiser concentration in percentage versus the relative density, for DOTP plasticiser and DINP plasticiser.

6.3.3.2.2.2 ESBO

Whilst only used in lower concentrations, it was important to investigate the influence of ESBO on the relative density of the PVC compound. Figure 6-17 shows the relationship between the plasticiser concentration and the relative density for both DOTP and DOTP with 5 PHR being replaced with ESBO plasticiser. As can be seen there is slight difference between the lines of fit for DOTP and DOTP with ESBO, demonstrating that for the relative density, the exchange of 5 PHR DOTP with 5 PHR ESBO would not cause significant issues for predicting the relative density. The impact of greater ESBO concentrations was investigated to account for versions of pPVC.

ESBO concentration versus the relative density is shown in Figure 6-18. It was observed that an increase in the ESBO concentration results in an increase in the relative density. Whilst the increase is only over a small range, it shows a strong correlation, with an R2 value of 0.9739. The density of ESBO plasticiser is 0.994 gcm^{-3} therefore an increase in the

relative density when the ESBO concentration is directly replacing DOTP is to be expected. Whilst a strong correlation is present, it is a limited impact and therefore for a predictive model will not be considered when calculating the relative density.

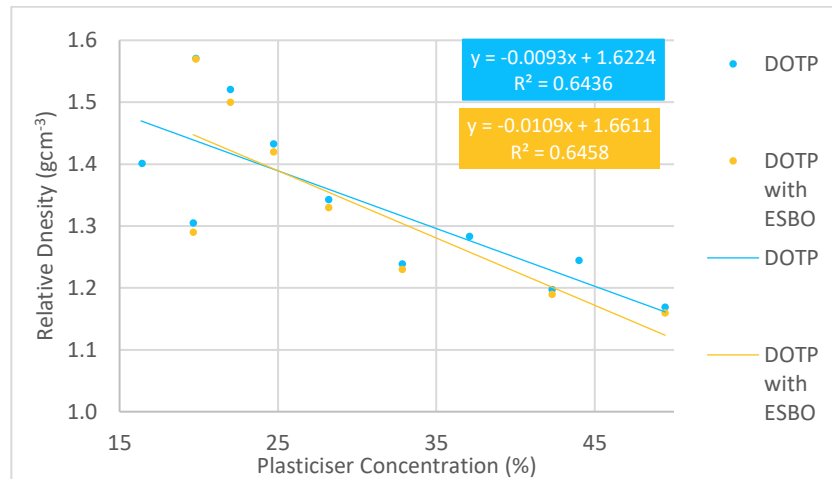


Figure 6-17: Graph showing the plasticiser concentration in percentage versus the relative density, for DOTP plasticiser and DOTP plasticiser with 5 PHR being replaced with ESBO plasticiser.

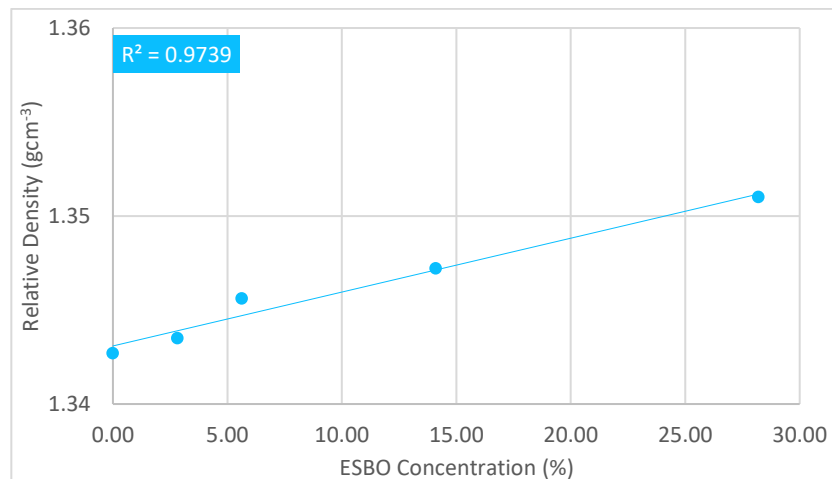


Figure 6-18: Graph showing how the relative density changes with an increase in the ESBO concentration (as a replacement for the DOTP at a 1:1 ratio) in PVC compound.

6.3.3.2.3 Filler Variations

As filler has been shown to have the greatest influence on the relative density the influence of different calcium carbonate types will provide information on whether the density will change with changes to this. Figure 6-19 shows the relative density for four different calcium carbonate filler types. GCC gives the highest relative density, with an increase in 0.01 gcm⁻³ compared to the other three filler types. This value is not significant from an industrial point of view. Figure 6-20 gives the filler concentration versus the relative density

for industrial grade calcium carbonate and precipitated calcium carbonate. Figure 6-20 shows similar correlations between the two fillers. For the proposed predictive model, the filler type will not need to be accounted for.

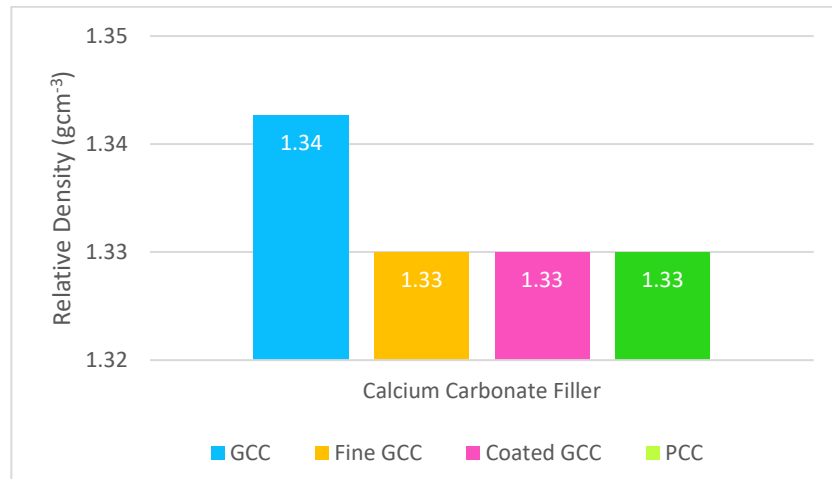


Figure 6-19: The relative density found when using different calcium carbonate fillers at the same concentration.

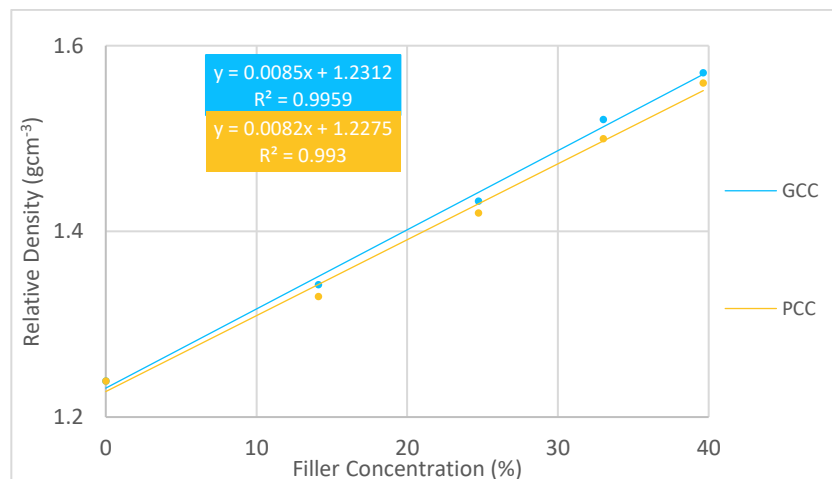


Figure 6-20: Graph showing the influence of two different calcium carbonates on the relative density with an increase in the concentration, in percentage.

6.3.3.2.4 Stabiliser Pack Variations

The stabiliser package concentration was changed between 1 – 5 PHR and the relative density was tested to determine whether this was something that had to be accounted for within the predictive model.

Figure 6-21 shows the influence of the stabiliser package concentration on the relative density. There was no observable difference in the relative density when increasing the stabiliser package concentration. This means that when calculating the relative density, the stabiliser package concentration does not need to be considered.

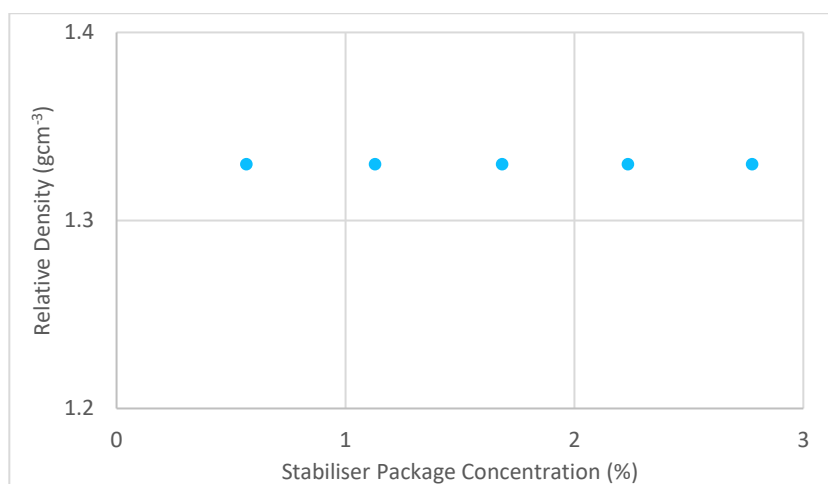


Figure 6-21: Graph showing the influence of the stabiliser pack concentration, in percentage, versus the relative density, in gcm⁻³.

6.3.3.2.5 Relative Density Conclusions

The alterations made to the raw materials within Phase 3 of this study had negligible effect on the relative density. The additive types which had the most significant impact on the relative density are the filler concentration, followed by the plasticiser concentration.

6.3.4 Congo Red Heat Stability

The Congo red heat stability test measures the time taken for enough hydrochloric acid to be released to change Congo red indicator paper from red to blue when heated. The presence of hydrochloric acid is due to the decomposition of the PVC resin within the compound. The following section explores the relationship between the Congo red heat stability and the different raw materials. Initially it looks at the data collected within phases 1 and 2, investigating only four raw materials (K70 resin, DOTP, GCC and a calcium-zinc stabiliser package). It then will look at the more varied raw materials used within phase 3 and their relationship with Congo red heat stability.

6.3.4.1 Phase 1 & 2

Figure 6-22 shows the relationship between the four base raw materials and the Congo red heat stability. The strongest correlation can be seen with DOTP; however, this is related to the decrease in PVC resin within the overall compound, leading to less hydrochloric acid

being reduced during degradation. The DOTP concentration was plotted against the Congo red heat stability in Figure 6-23, with the calcium carbonate concentration being used to separate the data further. Strong correlations were found at each calcium carbonate addition rate, indicating that an increase in concentration of both DOTP and calcium carbonate results in an increase in the Congo red heat stability.

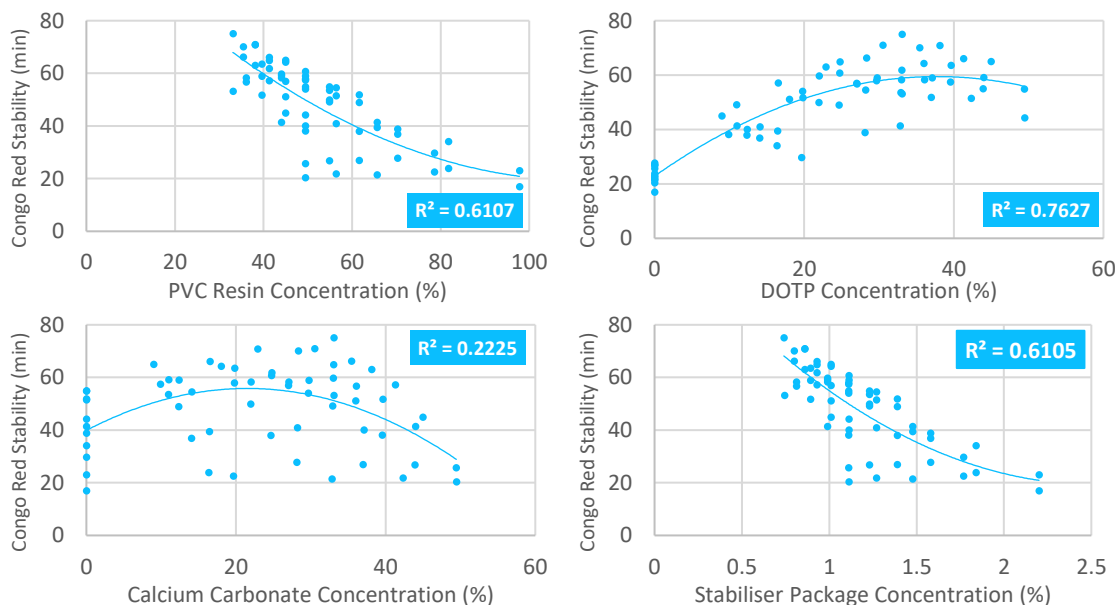


Figure 6-22: Graphs of the concentration of each raw material used within Phase 1 and Phase 2, are shown vs the average Congo red heat stability of each sample.

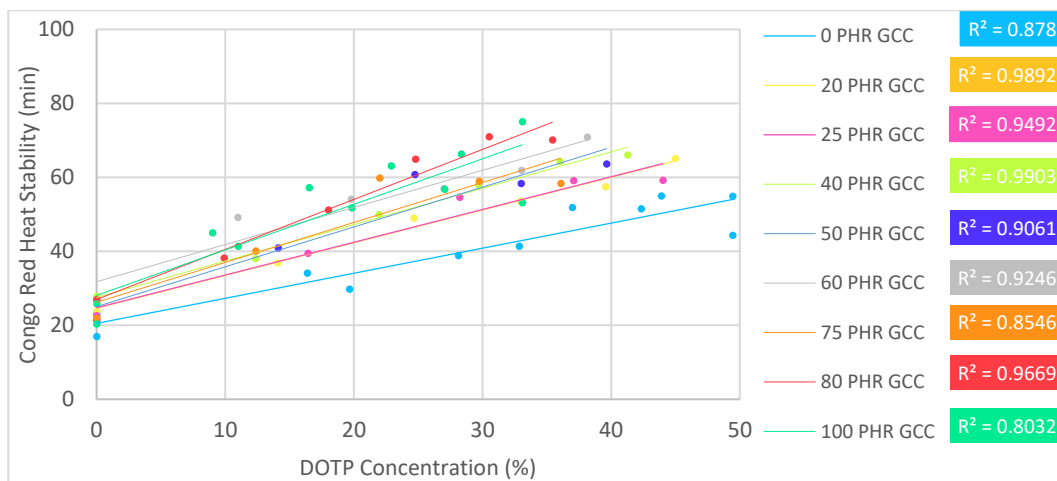


Figure 6-23: Graph showing the DOTP concentration, in percentage, vs the Congo red heat stability, with the data categorised by the calcium carbonate concentration, in PHR.

Overall, most of the relationships observed could be attributed to the dilution of PVC resin. However, DOTP has a larger observable effect on the heat stability, compared to calcium carbonate, suggesting that an additional interaction is taking place, and not just the dilution of the PVC resin present in the compound. There are two reasons for this.

1. The plasticiser is lubricating the material during the processing of the PVC compound, resulting in less degradation during processing, therefore when testing it must be heated longer to reach the point of hydrochloric acid release, prolonging the test time. Whereas when the adding filler to PVC compound the friction within the material increases as opposed to lubricating it.
2. The plasticiser is distributed more evenly throughout the material, and due to the plasticiser breaking the extended network of chain-to-chain dipole-induced forces present within the PVC compound, it allows the plasticiser to create a barrier between the PVC chains. This means that when the PVC chain is unzipping it is having a lesser effect on the PVC chains around it. In contrast, when the filler is added, it is not evenly distributed throughout the PVC compound and the chain-to-chain interactions are not influenced. Therefore, the only affect is diluting the overall compound.

6.3.4.2 Phase 3 – Raw material Variations

In this section the Congo red heat stability was compared with the raw materials used in phase 3 to determine any relationships and how they may affect a predictive model.

6.3.4.2.1 Resin Variations

As the test is measuring the decomposition of the PVC resin it is important to investigate whether a change in the resin type has any influence on the test times achieved.

Figure 6-24 shows the influence of the PVC K-value on the Congo red heat stability. A difference was observed between the samples, with K70 and K80 giving Congo red heat stability values over 55 minutes, whereas K66 and K100 gave values below 40 minutes. This is a difference of over 30%. A higher heat stability would be expected with a higher K-value, due to the lower number of chain ends, and therefore less chance of degradation initiation. The reason for the lower value found with K100 is that the material has gelled less and therefore is not fully combined, meaning that degradation can occur sooner.

Figure 6-25 shows the influence of the PVC resin concentration on the Congo red heat stability for both K70 and K100. A correlation was found for both K70 and K100, with the values found for K70 being significantly higher. This is something that would need to be considered when creating a predictive model, though the use of K100 within GP PVC is limited and tends to be used at a lower addition rate as a secondary resin.

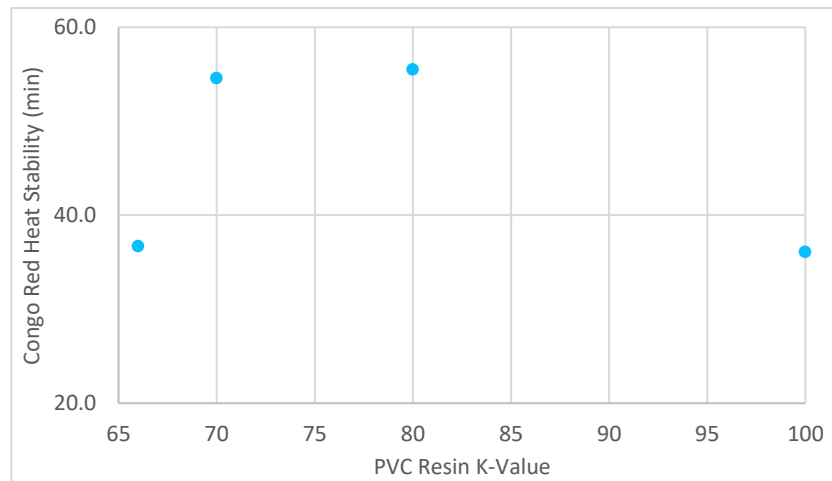


Figure 6-24: Graph of the Congo red heat stability found when changing the PVC resin K-Value.

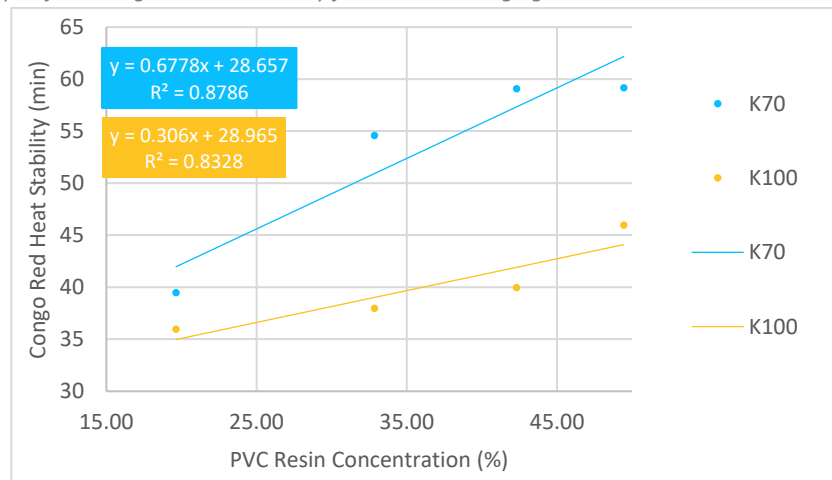


Figure 6-25: Graph showing the differences found in Congo red heat stability between K70 and K100 PVC resin with increasing DOTP concentration, in percentage.

6.3.4.2.2 Plasticiser Variations

The Congo red heat stability test detects the hydrochloric acid released from PVC once it reaches a certain saturation point. Whilst the plasticisers used in this study are not chlorinated, and therefore do not release hydrochloric acid, some plasticisers so have an influence on the stability of PVC compound.

6.3.4.2.2.1 DINP

The influence of changing the plasticiser type from DOTP to DINP on the Congo red heat stability was investigated.

Figure 6-26 gives a comparison of plasticiser concentration and Congo red heat stability for DOTP and DINP plasticisers. Whilst there is no evidence, academically, to suggest that a difference would be observed between the two plasticisers, the results show that DOTP gives a higher Congo red heat stability at every data point with the results for DINP being significantly lower. Further investigation into the difference observed here is needed to determine whether this is something that would need to be contemplated within the proposed predictive model.

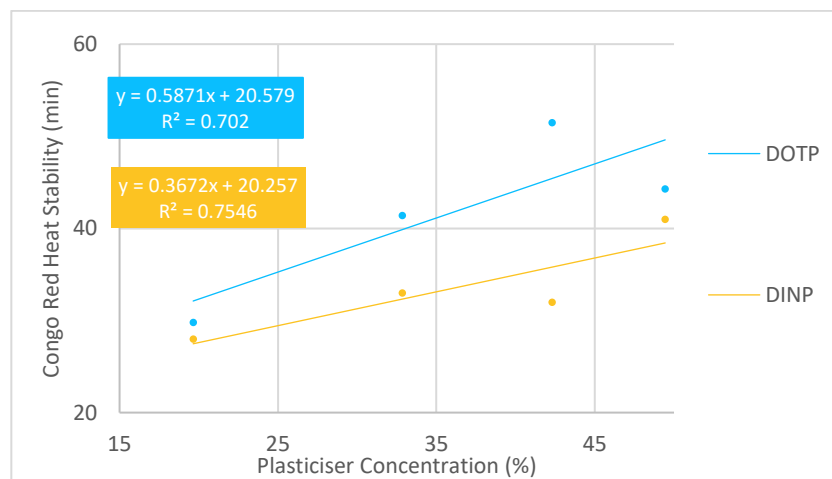


Figure 6-26: Graph showing the plasticiser concentration in percentage versus the Congo red heat stability, for DOTP plasticiser and DINP plasticiser.

6.3.4.2.2.2 ESBO

As well as being a secondary plasticiser, ESBO is frequently used as a secondary stabiliser.

This is because ESBO acts as an acid scavenger, with the epoxide group reacting with the hydrochloric acid released from PVC, neutralising its catalytic affects (Burns et al., 2023).

Figure 6-27 shows the plasticiser concentration versus the Congo red heat stability for DOTP and DOTP with ESBO. The results found for DOTP showed little correlation whereas those with 5 PHR being replaced with ESBO plasticiser displayed a clear correlation, with an R^2 value of 0.8103, suggesting ESBO has an impact on the Congo red heat stability.

Figure 6-28 shows the ESBO concentration versus the Congo red heat stability. A strong correlation can be seen, with an R^2 value of 0.996, showing that as the ESBO concentration increases so does the Congo red heat stability.

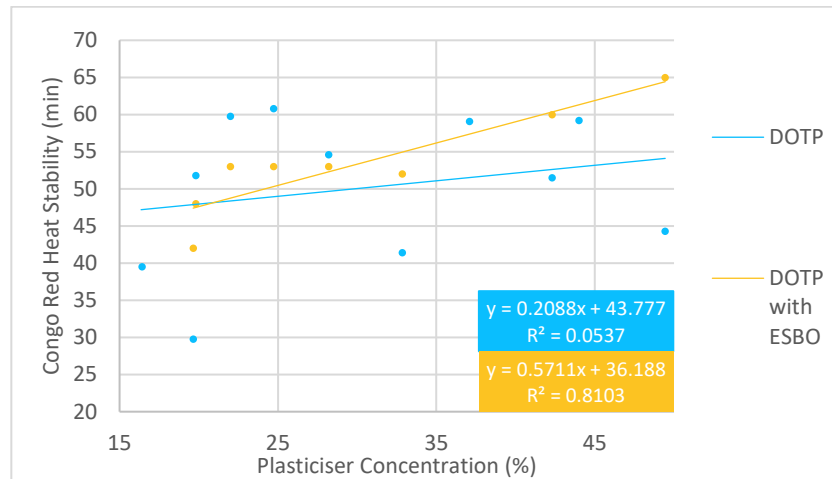


Figure 6-27: Graph showing the plasticiser concentration in percentage versus the Congo red heat stability, for DOTP plasticiser and DOTP plasticiser with 5 PHR being replaced with ESBO plasticiser.

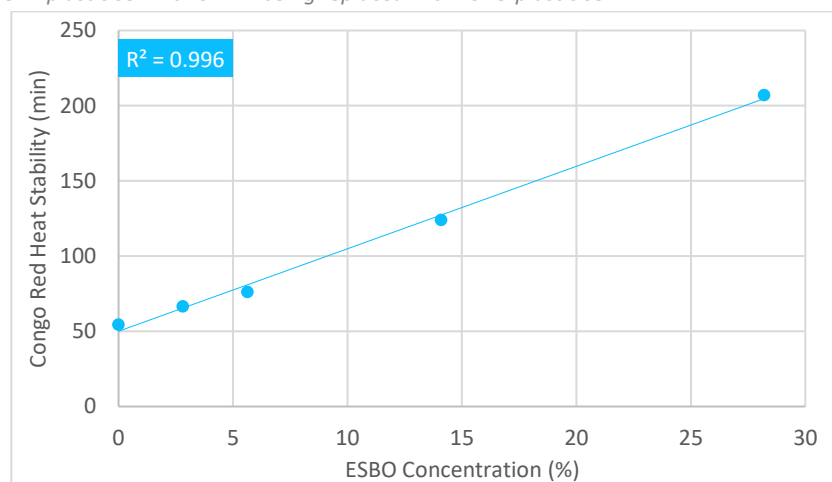


Figure 6-28: Graph showing how the Congo red heat stability changes with an increase in the ESBO concentration (as a replacement for the DOTP at a 1:1 ratio) in PVC compound.

6.3.4.2.3 Filler Variations

The influence of the calcium carbonate type on the Congo red heat stability was investigated. There is no evidence, academically, to suggest that the calcium carbonate interacts with the hydrochloric acid within PVC compound, however it was important to investigate any interactions for the predictive model.

Figure 6-29 shows the relationship between the Congo red heat stability and the four different calcium carbonate fillers evaluated. There is an increase in the Congo red heat stability when using the ultrafine GCC and coated GCC. The fine GCC has a smaller particle

size than standard GCC and coated GCC is coated with a lubricating agent. This would help with processing; this could account for the increase in the Congo red heat stability.

Figure 6-30 shows calcium carbonate concentration plotted against the Congo red heat stability in minutes. As seen within Figure 6-29 there is little difference found between the two types of calcium carbonate fillers.

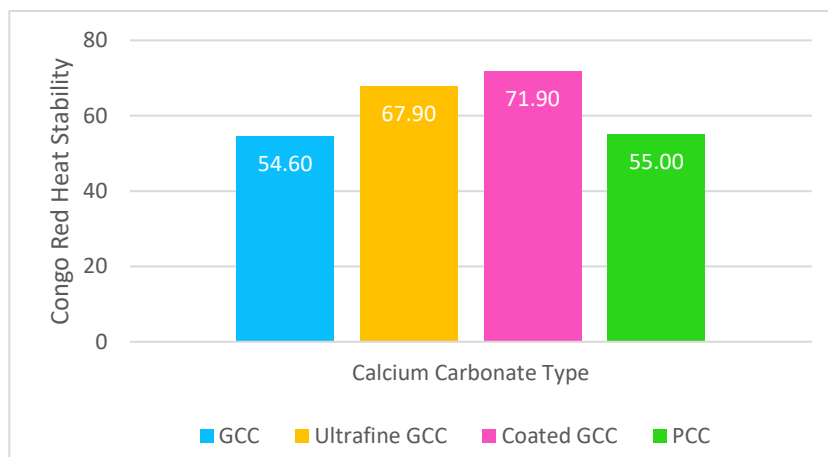


Figure 6-29: The Congo red heat stability found when using different calcium carbonate fillers at the same concentration.

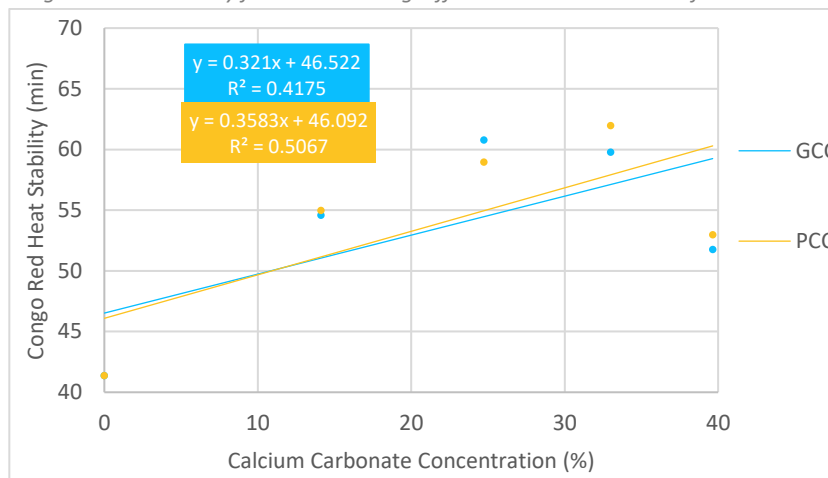


Figure 6-30: Graph showing the influence of two different calcium carbonates on the Congo red heat stability with an increase in the concentration, in percentage.

6.3.4.2.4 Stabiliser Pack Variations

As is discussed in section 2.3.3, the main defence against PVC degradation is the presence of a stabiliser package. Therefore, it can be assumed, that as the stabiliser package concentration increase so does the Congo red heat stability level. The exact relationship between the two was therefore investigated to see whether this was something that could be integrated into the proposed predictive model.

Figure 6-31 shows the relationship between the stabiliser package concentration versus the Congo red heat stability. As the stabiliser package concentration increases, so does the Congo red heat stability, showing a very strong relationship, with an R^2 value of 0.9996.

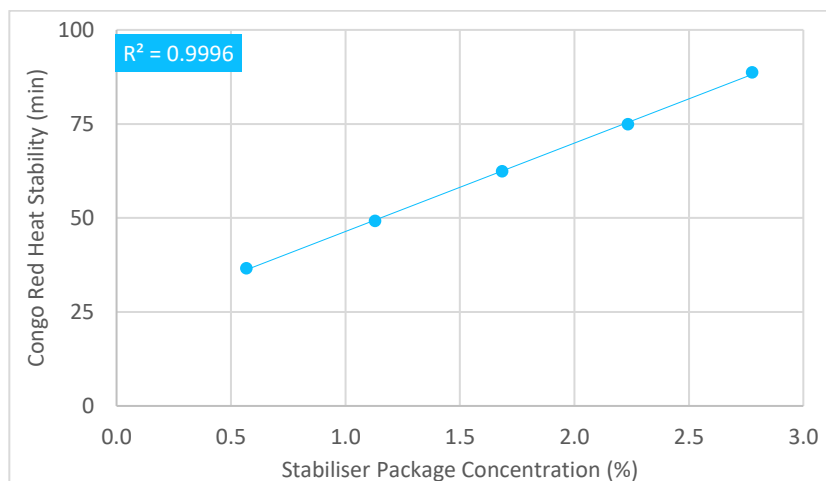


Figure 6-31: Graph showing the influence of the stabiliser pack concentration, in percentage, versus the Congo red heat stability, in minutes.

6.3.4.2.5 Congo Red Heat Stability Conclusions

Overall, the Congo red heat stability was impacted by several changes to the formulation of the PVC compound. When looking at phase 1 and 2 the main influence is due to the dilution of the PVC resin within the compound. Within Phase 3 the largest influence is observed when the stabiliser package concentration is increased and when the ESBO concentration is increased. In addition, influences can be seen when making alterations to the resin and filler types.

It is however worth noting, that out of all the industrial tests completed in this study, the Congo red heat stability is susceptible to ambiguity. This is because it relies upon the human determination of when the Congo red paper has turned blue, and therefore this is subject to bias.

6.3.5 Tensile Strength

The following section explores the relationship between the tensile strength and the different raw materials. Initially it looks at the data collected within phases 1 and 2,

investigating at only four raw materials (K70 resin, DOTP, GCC and a calcium-zinc stabiliser package). It then will look at the more varied raw materials used within phase 3 and their relationship with tensile strength.

6.3.5.1 Phase 1 & 2

Tensile strength testing measures the maximum stress that a material can take before breaking, this is an important property for pPVC as it is frequently used in high stress applications, such as in cables and gaskets. Figure 6-32 shows the relationship between the concentration of the four bases and the tensile strength of the PVC compound. DOTP shows the strongest correlation, with the tensile strength decreasing as the DOTP concentration increases.

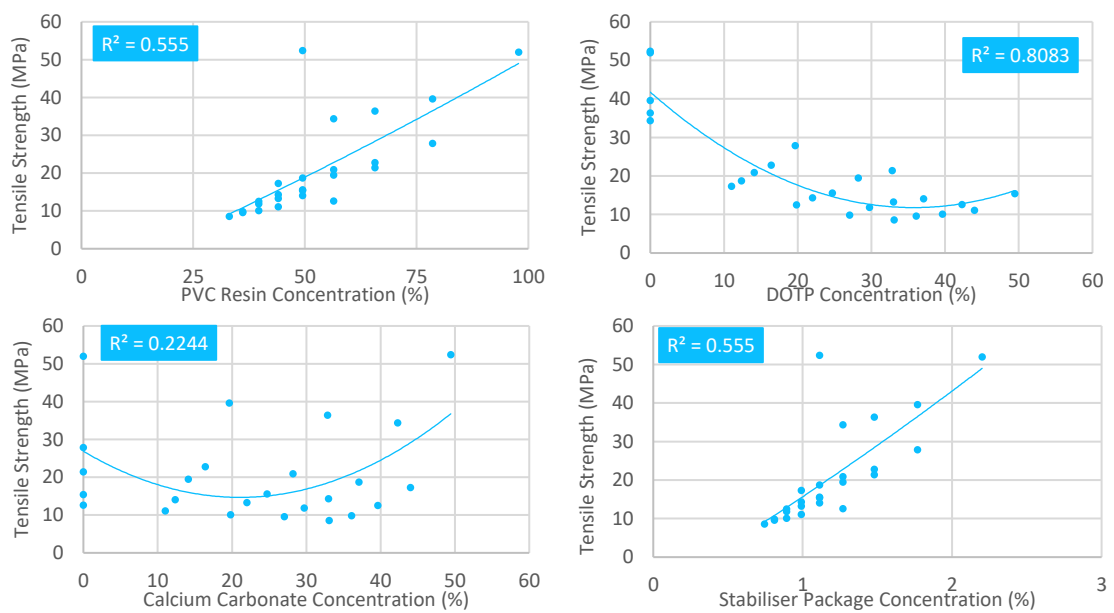


Figure 6-32: Graphs of the concentration of each raw material used within Phase 1 and Phase 2, are shown vs the average tensile strength of each sample.

In Figure 6-33 the DOTP concentration is shown versus the tensile strength, with the data being split by the calcium carbonate concentration. A strong correlation is found at each concentration, with R^2 values of greater than 0.8497. The gradient of the lines of fit at each calcium carbonate concentration have a similar slope, showing a pattern in the overall data with the main difference being the intercept.

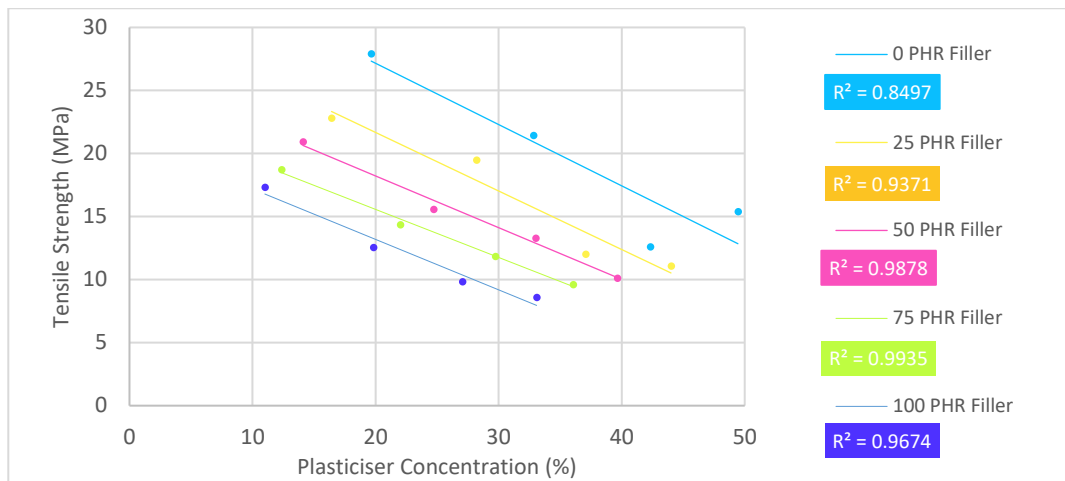


Figure 6-33: Graph showing the DOTP concentration, in percentage, vs the tensile strength, with the data categorised by the calcium carbonate concentration, in PHR.

In this section, it is demonstrated that filler and plasticiser concentration can be used to predict the tensile strength. There are stark differences when there are lower concentrations of plasticiser and when there is no filler present, therefore this would need to be accounted for if the results were to be used to predict the tensile strength from the raw material concentration.

6.3.5.2 Phase 3 – Raw material Variations

In this section the tensile strength was compared with the raw materials investigated in phase 3 to determine the relationships and how they may affect a predictive model.

6.3.5.2.1 Resin Variations

The influence of the PVC resin type on the tensile strength is investigated within this section. Within certain applications, such as wires, higher K-value resins are used to impart additional mechanical properties, such as improved abrasion and tensile properties. Therefore, differences would be expected in the tensile strength.

Figure 6-34 shows the PVC K-value versus the tensile strength. The data points show an increase in the tensile strength with increasing K-value between K66 and K80 resin, however the value found for K100 is lower than K80. This is something that could be put down to the degree of gelation of the PVC compound made with the K100 resin, if the material is not fully gelled then this could result in a lower tensile strength result.

Figure 6-35 shows the plasticiser concentration versus the tensile strength for formulations using K70 and K100 PVC resin, in an unfilled formulation. Strong correlations were found for both K70 and K100 resin, with a slight increase in the tensile strength was observed across all data points other than those at the highest plasticiser concentration. This difference will have to be considered for a predictive model.

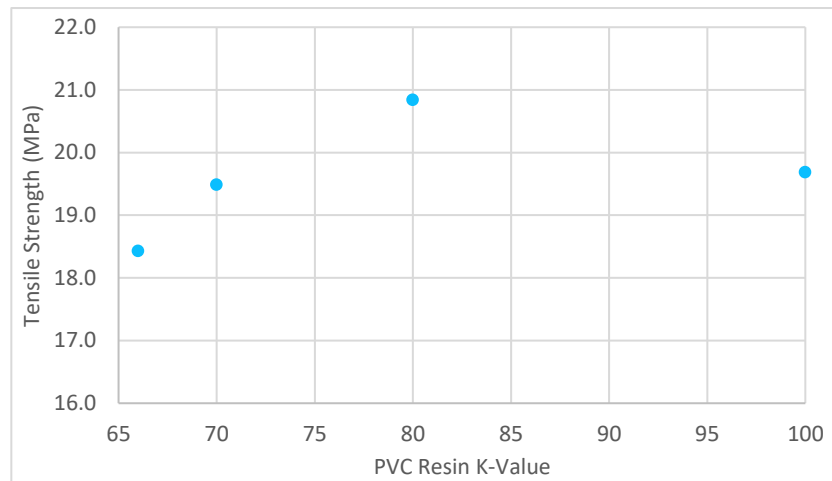


Figure 6-34: Graph of the tensile strength found when changing the PVC resin K-Value.

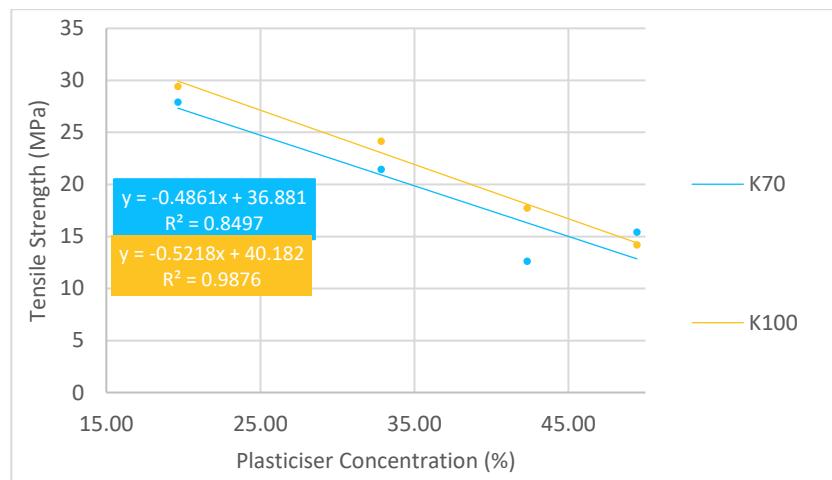


Figure 6-35: Graph showing the differences found in tensile strength between K70 and K100 PVC resin with increasing DOTP concentration, in percentage.

6.3.5.2.2 Plasticiser Variations

As with the resin type, different plasticisers are sometimes used to impart additional properties in pPVC. The plasticisers used within this study are not expected to provide significant changes to the tensile properties, however this has been investigated to determine any differences that are present.

6.3.5.2.2.1 DINP

The influence of changing the plasticiser type from DOTP to DINP on the tensile strength was investigated, to determine whether this was something that would need to be accounted for within a predictive model.

Figure 6-36 shows the plasticiser concentration versus the tensile strength for both DOTP and DINP. The results found show similar correlations for both plasticisers, with a strong correlation for both DOTP and DINP being observed, with R^2 values of 0.8497 and 0.9704, respectively. As the results are so similar the use of DOTP/DINP will not need to be considered for a predictive model.

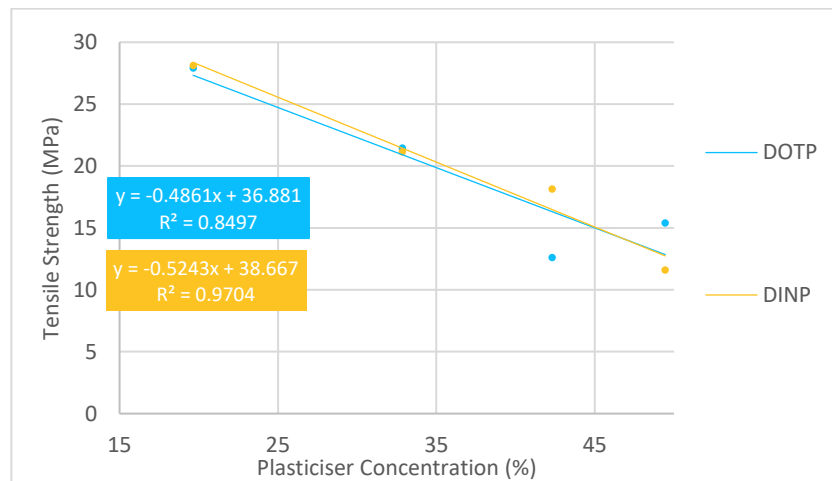


Figure 6-36: The plasticiser concentration in percentage versus the tensile strength, for DOTP and DINP plasticiser.

6.3.5.2.2.2 ESBO

ESBO, both at a loading of 5 PHR in DOTP and as the primary plasticiser, and its influence on the tensile strength was investigated to determine whether this needed to be accounted for within a predictive model.

Figure 6-37 shows the plasticiser concentration, for DOTP and DOTP with ESBO, versus the tensile strength. No strong correlation can be found from these data sets. However, despite this, the trend lines constructed are similar and many of the datapoints produced comparable results. These results demonstrate that for a predictive model, when calculating the tensile strength, low concentrations of ESBO as an additional plasticiser will

not need to be differentiated from the overall plasticiser concentration. Figure 6-38 shows the ESBO concentration versus the tensile strength in a formulation containing 50 PHR total plasticiser. The largest difference found is 5.8% with all other data points falling within this range. Therefore, the differences observed can be put down to test and sample variation.

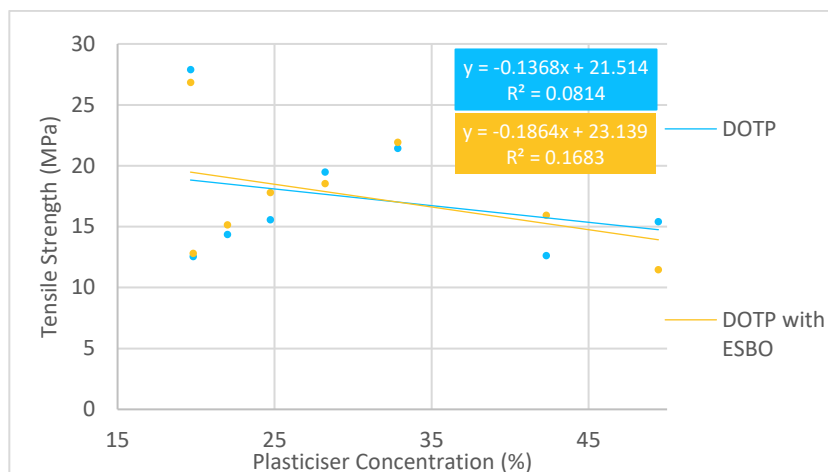


Figure 6-37: Graph showing the plasticiser concentration in percentage versus the tensile strength, for DOTP plasticiser and DOTP plasticiser with 5 PHR being replaced with ESBO plasticiser.

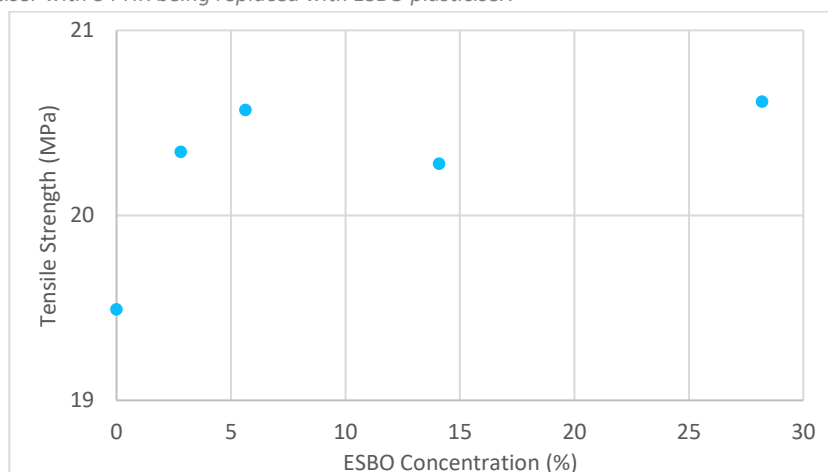


Figure 6-38: Graph showing how the tensile strength changes with an increase in the ESBO concentration (as a replacement for the DOTP at a 1:1 ratio) in PVC compound.

6.3.5.2.3 Filler Variations

In this section the influence of the calcium carbonate filler type on the tensile strength was investigated. Figure 6-39 shows the tensile strength values found for each calcium carbonate type used. The results show that the four calcium carbonate types were within 1.5 MPa and therefore within standard test error. However, it is worth noting that the three non-GP calcium carbonates gave much closer results, suggesting that their smaller particle size and additional features may be having an influence.

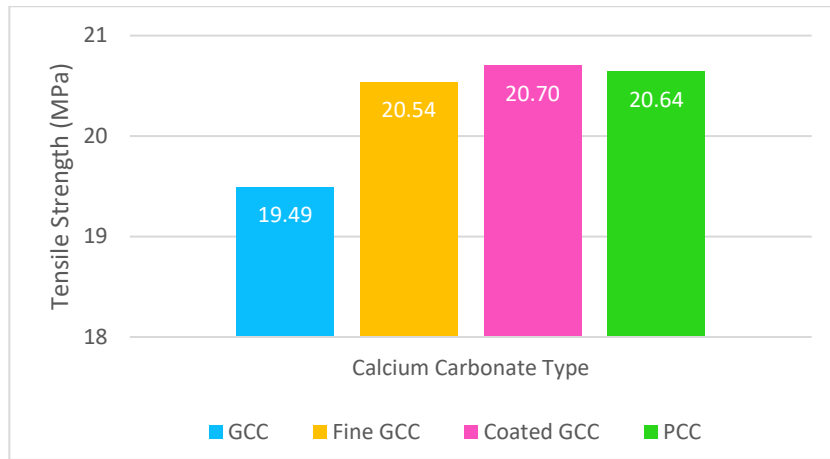


Figure 6-39: Tensile strength found when using different calcium carbonate fillers, the same concentration.

Figure 6-40 shows the filler concentration versus the tensile strength, for industrial grade calcium carbonate and precipitated calcium carbonate. Both calcium carbonate types gave strong correlations, with the tensile strength decreasing as the calcium carbonate concentration increased. The two calcium carbonates provide comparable results, with a greater difference being found as the concentration increases, with the precipitated calcium carbonate giving lower values. For a predictive model this is something that would have to be considered, however as the difference is only at higher concentrations it could be that only an advisory statement is required.

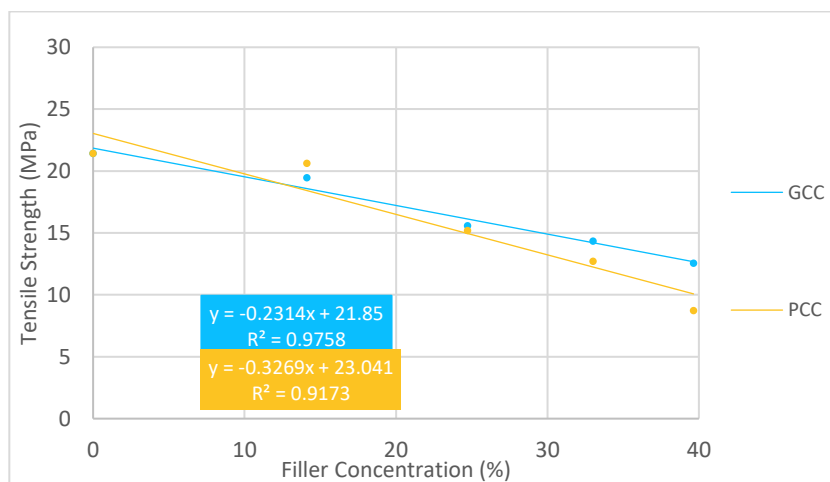


Figure 6-40: Graph showing the influence of two different calcium carbonates on the tensile strength with an increase in the concentration, in percentage

6.3.5.2.4 Stabiliser Pack Variations

The influence of the stabiliser package concentration on the tensile strength was investigated in Figure 6-41. A slight correlation can be seen, with the tensile strength

decreasing as the stabiliser package concentration increases. This is because there is a difference in the degree of gelation due to increased lubrication of the PVC compound. However, because this difference is only over 2 MPa, close to the expected test variation, it will not be considered in a predictive model.

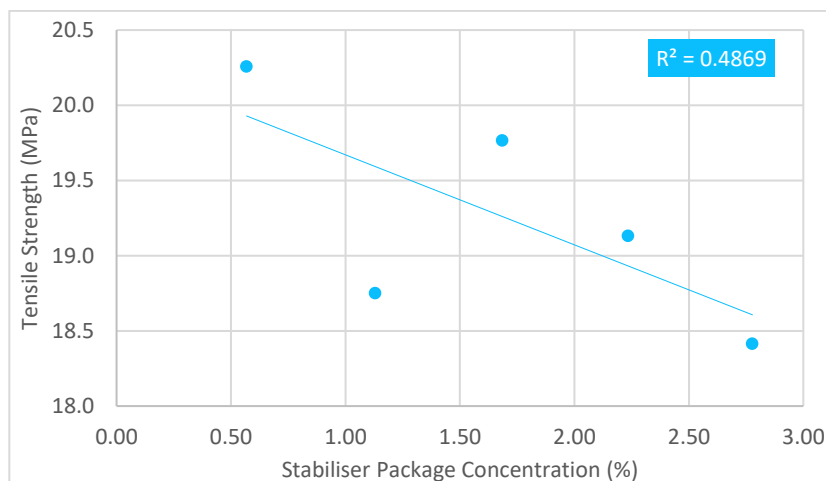


Figure 6-41: The influence of the stabiliser pack concentration, in percentage, versus the tensile strength in MPa.

6.3.6 Elongation at Yield

The following section explores the relationship between the elongation at yield and the different raw materials. Initially it looks at the data collected within phase 2, investigating at only four raw materials (K70 resin, DOTP, GCC and a calcium-zinc stabiliser package). It then will look at the more varied raw materials used within phase 3 and their relationship with elongation at yield. Elongation testing for phase 1 and 2 was completed on two different instruments, therefore the results presented in this section were based only on the phase two data, which was collected on an instrument that did not require manual measurement, therefore providing a higher accuracy result.

6.3.6.1 Phase 2

The elongation at yield is measured alongside the tensile strength when testing the tensile properties. It is the measure of how far a material can be stretched, at a constant rate, before it breaks.

In this section the raw material concentrations of the phase 2 samples and their corresponding elongation at yield were measured. The graphs for each base raw material compared to the elongation at yield are shown in Figure 6-42. DOTP gave the strongest correlation, with an R^2 value of 0.8858, whilst all other raw materials demonstrated limited correlation.

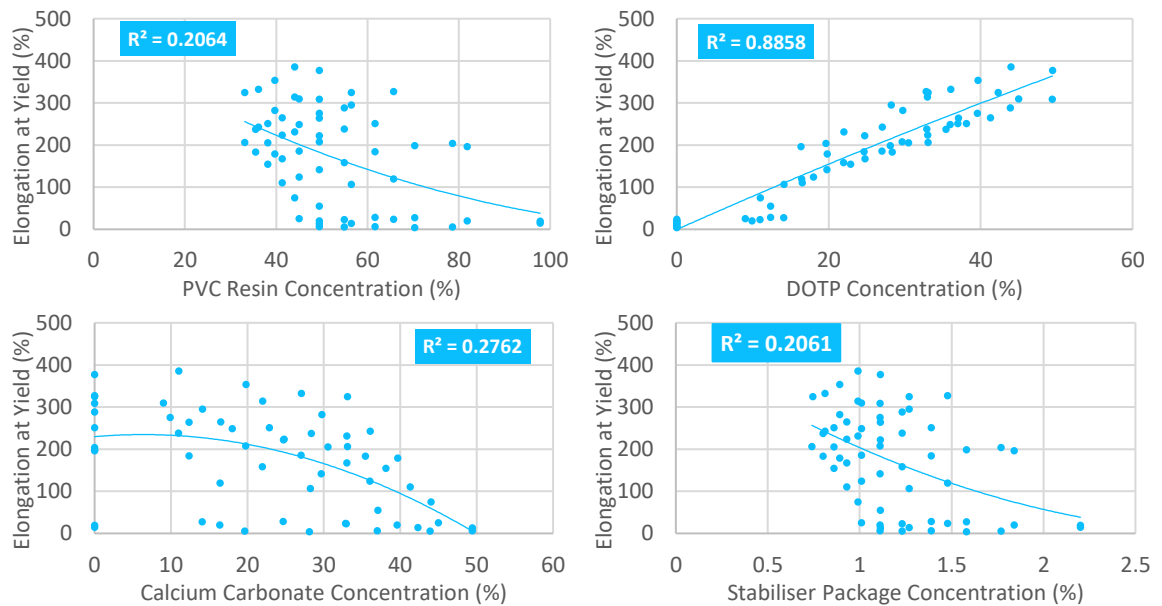


Figure 6-42: Graphs of the concentration of each raw material used within Phase 1 and Phase 2, are shown vs the average elongation at yield of each sample.

Figure 6-43 shows the DOTP concentration versus the elongation at yield, further categorised by the calcium carbonate concentration. At all calcium carbonate concentrations, a strong correlation was found, with the lowest R^2 value being 0.8852. Samples containing calcium carbonate gave similar trend lines. The trend line found for those samples that did not contain calcium carbonate show a lower gradient, suggesting that the DOTP concentration is having a greater effect on the elongation in the presence of calcium carbonate filler.

The results from this section have demonstrated that plasticiser and filler concentrations can be used to predict the elongation of pPVC, with strong linear correlations being observed.

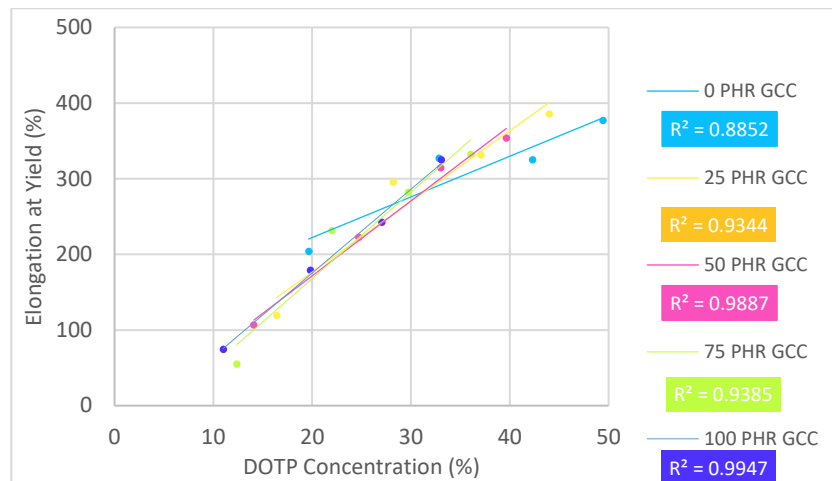


Figure 6-43: Graph showing the DOTP concentration, in percentage, vs the elongation, with the data categorised by the calcium carbonate concentration, in PHR.

6.3.6.2 Phase 3 – Raw material Variations

In this section the elongation at yield was compared with the different raw materials investigated in phase 3 to determine the relationships present and how they may affect a predictive model.

6.3.6.2.1 Resin Variation

In this section the influence of the resin variation on the elongation at yield is investigated (Figure 6-44). A strong correlation can be observed between the elongation at yield which decreases as the PVC resin K-value increases, with an R² value of 0.9222 being found. One explanation for this is the variation in degree of gelation of the material between different K-values. Materials using lower K-values gel faster than those using higher K-values, therefore providing a higher elongation at yield when the materials are processed at the same temperatures. This is something that would need to be considered when compiling a predictive model as a significant difference can be seen.

Figure 6-45 shows the plasticiser concentration, versus the elongation at yield, for formulations containing K70 and K100. Strong correlations were found for both resins, with the K70 providing higher elongation at yield values. Again, this difference could be a result of variations in the degree of gelation of the material, with K100 resin requiring more work

to achieve a fully gelled material. This is something that will need to be considered within a predictive model.

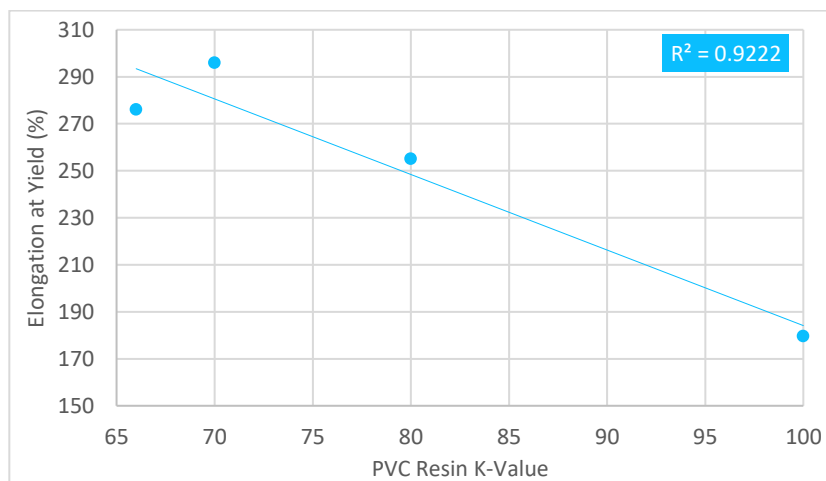


Figure 6-44: Graph of the elongation at yield found when changing the PVC resin K-Value.

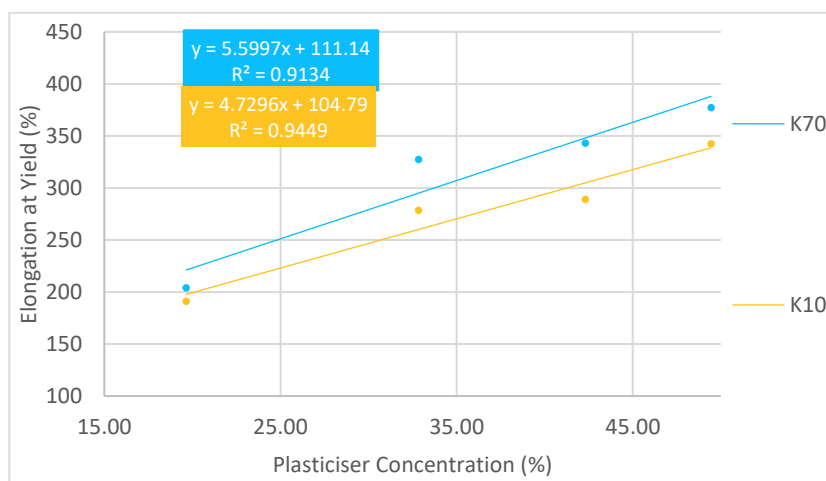


Figure 6-45: Graph showing the differences found in elongation at yield, between K70 and K100 PVC resin, with increasing DOTP concentration, in percentage.

6.3.6.2.2 Plasticiser Variations

As was discussed in section 6.3.5.2.2, different plasticisers are sometimes used to impart additional properties in pPVC. The plasticisers used within this study are not expected to provide significant changes to the tensile properties, however this has been investigated to determine any differences that are present.

6.3.6.2.2.1 DINP

The influence of the plasticiser type versus the elongation at yield was investigated, the change from DOTP to DINP can be seen in (Figure 6-46). Overall, both presented strong correlations, with DINP plasticiser giving slightly higher results as the plasticiser

concentration increases. The difference observed at the highest plasticiser concentration are on the cusp of what would be considered as within a QC specification. For a predictive model, this would potentially be covered by an advisory statement.

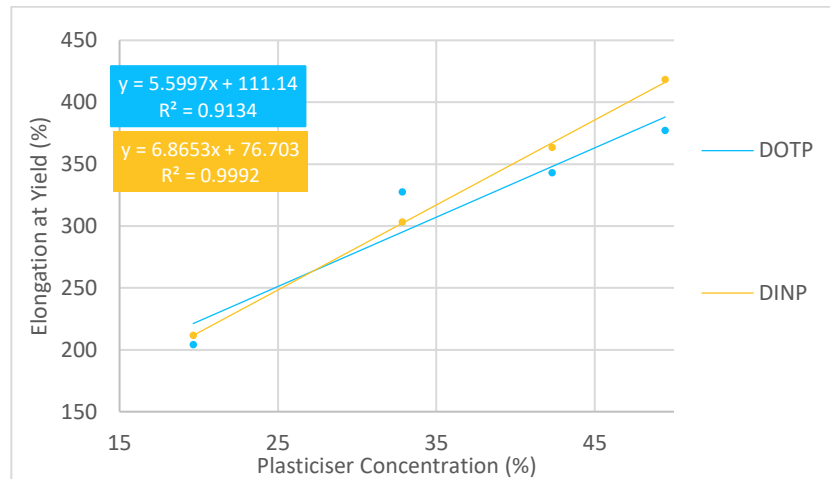


Figure 6-46: Graph showing the plasticiser concentration in percentage versus the elongation at yield, for DOTP and DINP.

6.3.6.2.2.2 ESBO

The influence ESBO, both at 5 PHR with DOTP and in varying levels in a 50 PHR plasticiser pPVC compound, on the elongation at yield was investigated.

Figure 6-47 shows the plasticiser concentration versus the elongation at yield for DOTP plasticiser and DOTP plasticiser with 5 PHR being replaced with ESBO plasticiser. Both plasticisers provide strong correlations with a similar data points and trendlines being observed. For a model, small additions of ESBO, will not be considered when looking at the plasticiser concentration.

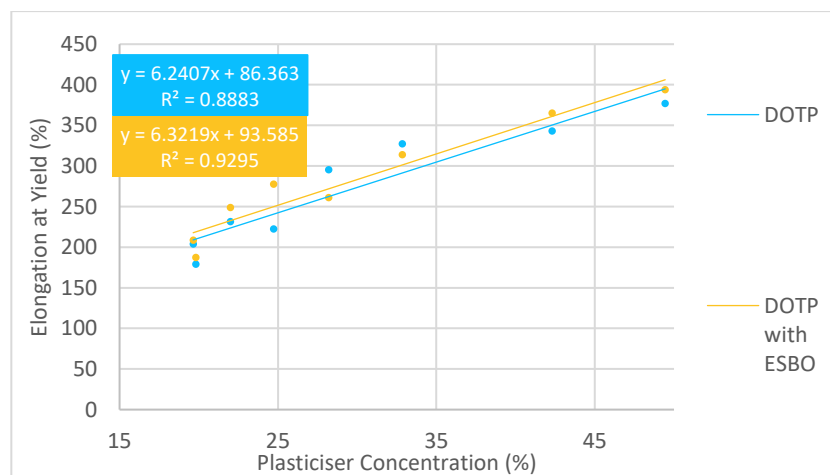


Figure 6-47: Graph showing the plasticiser concentration in percentage versus the elongation at yield, for DOTP plasticiser and DOTP plasticiser with 5 PHR being replaced with ESBO plasticiser.

Figure 6-48 shows the ESBO concentration versus the elongation at yield. Overall, following the initial addition of ESBO within the pPVC, the addition of any level of ESBO appears to have no significant influence, with all values falling within a 10% elongation at yield range. Therefore, for a predictive model this will not be considered.

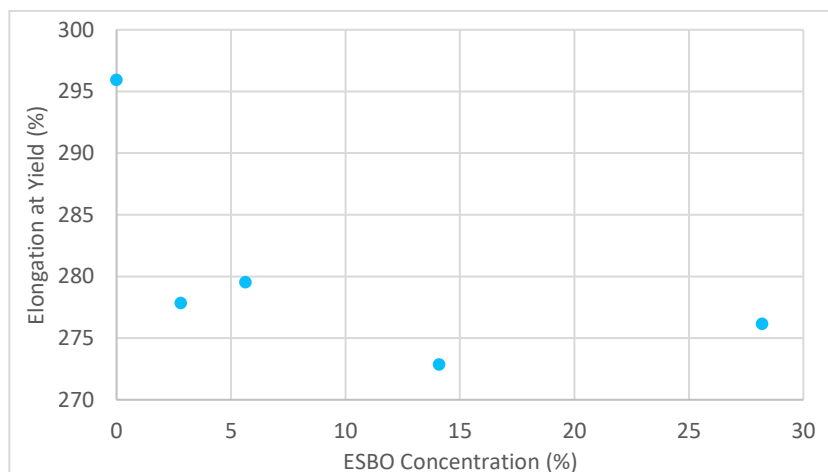


Figure 6-48: Graph showing how the elongation at yield changes with an increase in the ESBO concentration (as a replacement for the DOTP at a 1:1 ratio) in PVC compound.

6.3.6.2.3 Filler Variations

The influence of the different calcium carbonate concentrations on the elongation at yield was investigated.

Initially, in Figure 6-49 the elongation at yield for four different calcium carbonate types was investigated. The differences seen would all be within the expected test variation within industry. However, the GCC does give a value that stands out compared with the other three values. This would need to be investigated further to determine whether it is significant due to the closeness to the other values. Based on this data, a predictive model would not need to consider the calcium carbonate filler type when calculating the elongation at yield.

Figure 6-50 shows the influence of the filler concentration on the elongation at yield for both industrial grade calcium carbonate and precipitated calcium carbonate. Both calcium carbonates gave strong correlations, with the industrial grade calcium carbonate giving a slight increase in the elongation over the precipitated calcium carbonate. Other than at

the highest calcium carbonate concentration, all results are within expected test variation, therefore for a predictive model only an advisory statement would need to be considered for higher calcium carbonate concentrations.

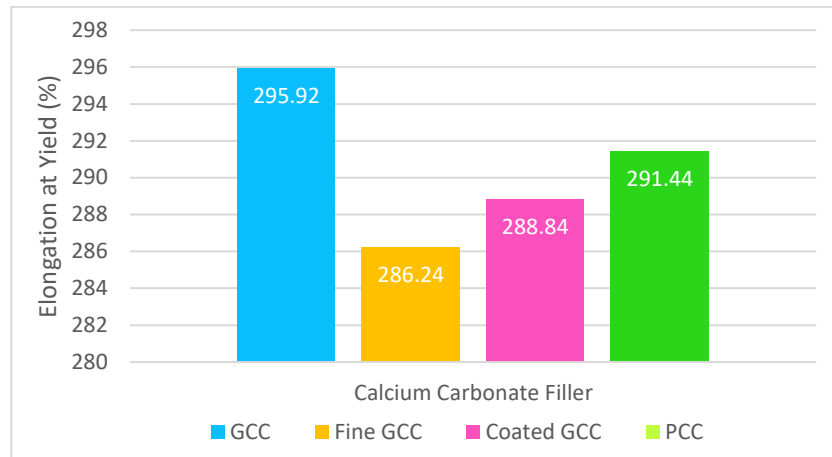


Figure 6-49: The elongation at yield found when using different calcium carbonate fillers at the same concentration.

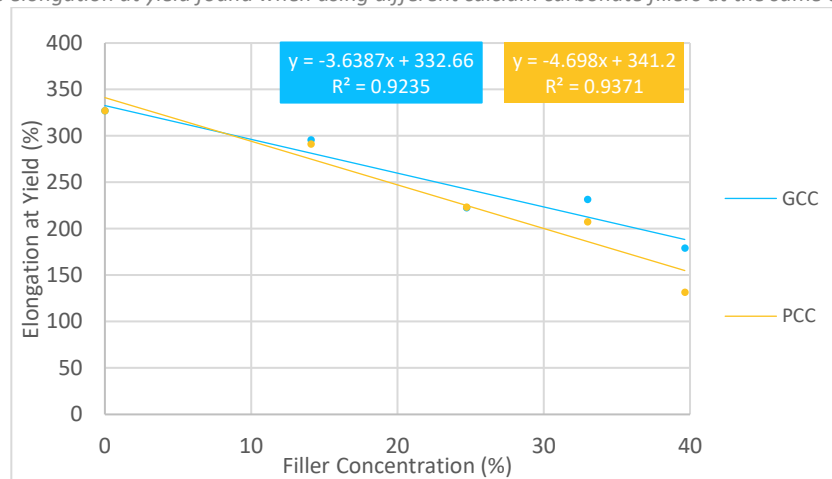


Figure 6-50: Graph showing the influence of two different calcium carbonates on the elongation at yield with an increase in the concentration, in percentage.

6.3.6.2.4 Stabiliser Pack Variations

The stabiliser package concentration versus the elongation at yield can be seen in Figure 6-51. Differences can be observed between the datapoints; however, all are within 10% of each other, with no overall correlation being found. This suggests that the results found for the stabiliser package are due to either sample preparation or processing rather than due to a notable change in the material.

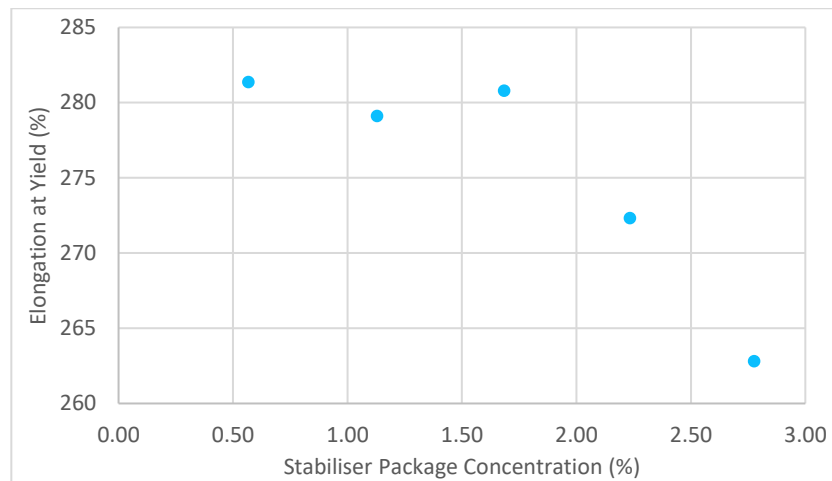


Figure 6-51: Graph showing the influence of the stabiliser pack concentration, in percentage, versus the elongation at yield, in percentage.

6.3.6.2.5 Elongation at Yield Conclusion

The concentration of plasticiser has, by far, the largest influence on the elongation at yield of a PVC compound. As the plasticiser is decreasing the glass transition temperature of the material and making it “rubberier”, therefore it makes sense for the material to then become more elastic, giving a greater elongation at yield. Calcium carbonate also had an influence on the elongation, mostly when it was and was not present, rather than at varying concentrations. Changes to the raw material types had minimal impacts on the results and therefore will only be considered as advisories for the predictive model.

6.3.7 Industrial Testing Conclusion

Overall, the industrial testing has provided the following conclusions.

1. Plasticiser has the greatest influence on the tests completed, when the calcium carbonate concentration is considered with this, strong correlations can be observed.
2. Of the five tests completed, Congo red heat stability gave the most complex results. In part this is due to the complexity of the stability of PVC and the minimal additional of stabiliser package required to change this.
3. The results found have proven that correlations exist between the base raw materials and the mechanical/physical industry-related tests completed, and that therefore, with

careful consideration, a predictive model could be created that allows for the calculation of the industrial test values from the raw material concentrations.

The following section will investigate the spectroscopic results found with the raw material changes in Phases 1, 2 and 3.

6.4 Spectroscopic Testing

As was discussed in Chapter 5 - Spectral Analysis, all spectral analysis was completed using the custom software, as described in Chapter 4 – Methodology. The Raman peak areas did not show useful correlations with the raw material concentration. Therefore, whilst Raman testing was completed on all samples produced, it will not be used within the predictive model and will not be discussed here.

6.4.1 FT-IR Spectroscopy

Whilst the industrial testing completed so far is of great importance to the predictive model, to make it truly impactful it is important that there is a quick and effective way to predict the raw material levels present within a pPVC sample. Therefore FT-IR was selected as a non-destructive and fast technique to quantify the raw material levels within the compound.

The following section will firstly explore the relationships found between the four raw materials (K70 PVC resin, DOTP plasticiser, GCC filler and calcium-zinc stabiliser) and the data from FT-IR following curve fitting using FTIR-fitting.

6.4.1.1 Phase 1 & 2

Following the testing completed in Chapter 5 - Spectral Analysis, using the data from Phase 1, this section takes the data used in both phases 1 and 2 and determines the relationships present. Unlike with Chapter 5 the data here was normalised to 1 and not to percentage. In total, within phases 1 and 2, 334 spectra were analysed. The results of which can be seen in Figure 6-52, which gives four graphs showing the raw material concentrations for

the four base raw materials versus the normalised peak height for each raw material as identified in Chapter 5. For the PVC resin, a quadratic correlation was determined, as the concentration increases the peak height increases at a steeper rate. For the other three raw materials a linear correlation was deemed most suitable. For PVC resin, plasticiser and calcium carbonate a strong correlation can be found, with all giving an R^2 value greater than 0.877, however for the stabiliser package no correlation is present. These results suggest that the deconvoluted peak height is proportional to raw material concentration and therefore can be used in the predictive model. As can be seen a linear relationship was found for the plasticiser and calcium carbonate, whereas a quadratic trendline was found for PVC resin. As the stabiliser package concentration cannot be predicted using the spectroscopic data, an alternative system will have to be used for the prediction of this with a predictive model.

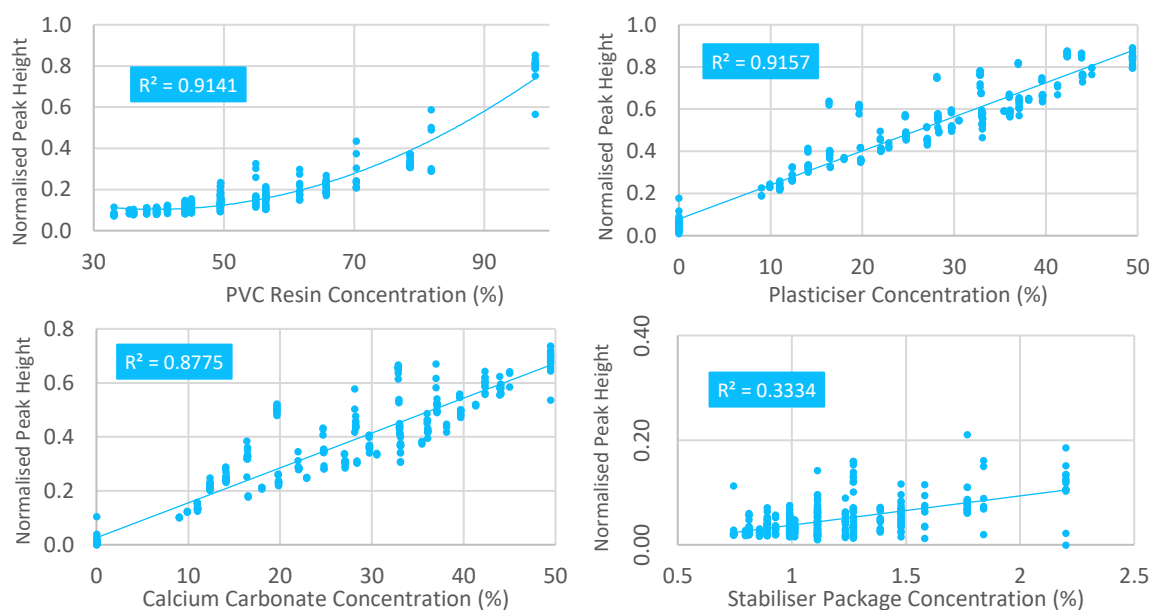


Figure 6-52: Graphs of the concentration of each raw material used within Phase 1 and Phase 2, are shown vs the normalised peak height.

6.4.1.2 Phase 3 – Raw material Variations

Whilst the results found in phases 1 and 2 are to be used to create the basis of the predictive model, within Phase 3 the influence of the additional raw materials on the FT-IR spectra and the spectral analysis software, FTIR-fitting, was investigated.

6.4.1.2.1 Resin Variations

To investigate the influence that variation in resin type would have, changes in peak height was plotted against different K-values.

Figure 6-53 shows the change in the normalised peak height as the K-Value increases. A linear correlation is observed, with an R^2 value of 0.7838. The value found for K80 is lower than expected from the pattern observed between the other resins. The largest difference found between the points is 0.041, which is like the variation seen between the same PVC resins concentrations found in Figure 6-52.

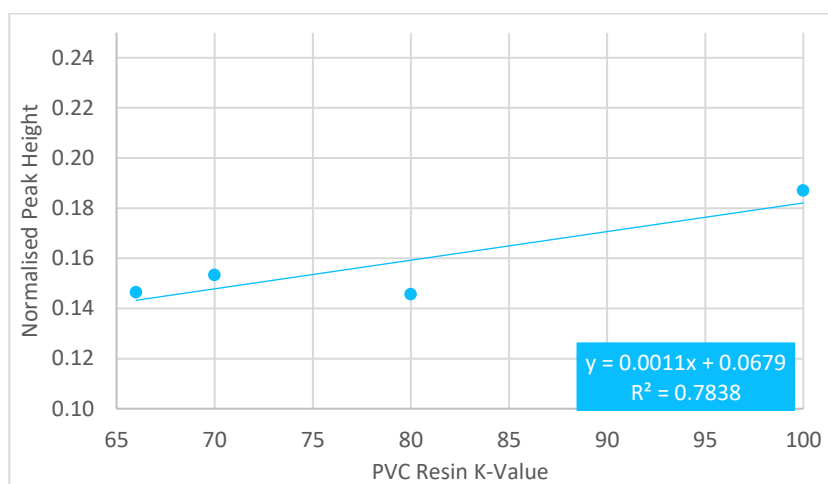


Figure 6-53: Graph of normalised peak height plotted against PVC resin K-value.

Figure 6-54 shows the PVC resin concentration versus the normalised peak height for K70 and K100. A strong correlation can be found for both K70 and K100, with R^2 values of 0.8768 and 0.9614, respectively. A difference was found between the two K-values, with a similar gradient being found for both K-values and a difference in the intercept of 0.1376. As the data gives lines with high correlations, with gradients of a similar magnitude, it would be possible to account for this within a model using a correction factor. However, it would first need to be determined which resin was present, something that could prove difficult in practice as PVC resins tend to look identical on FT-IR. It is worth noting that the use of K100 is limited within the PVC industry, and is often used in lower concentrations, therefore the difference observed here will have a limited effect.

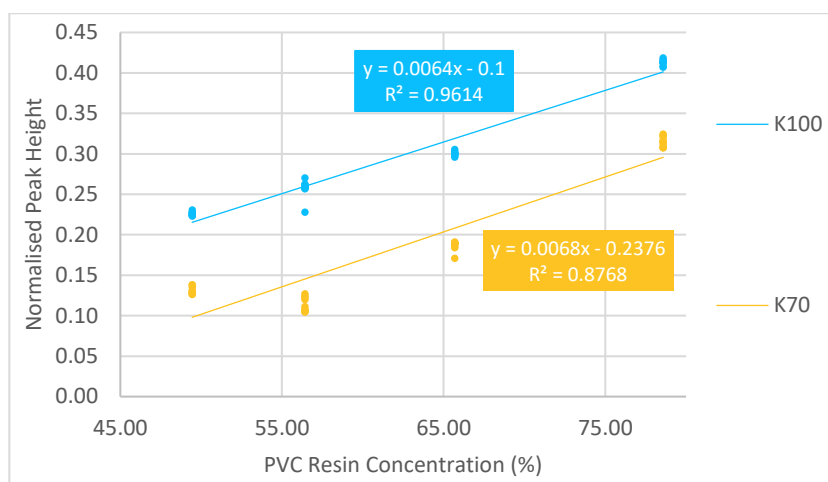


Figure 6-54: Graph of normalised peak high versus percentage PVC resin concentration.

6.4.1.2.2 Plasticiser Variations

To investigate the influence that variation in plasticiser type would have, changes in peak height was plotted against different plasticisers and plasticiser combination.

6.4.1.2.2.1 DINP

As DINP has a different structure to DOTP the effectiveness of the FTIR-fitting software needed to be assessed to investigate whether the fitting software could still be used to determine the plasticiser concentration within the pPVC.

In Figure 6-55 the plasticiser concentration was plotted versus the normalised peak height for DINP and DOTP plasticisers. Both DINP and DOTP gave strong correlations, with R^2 values of 0.9447 and 0.8431, respectively. A difference in the intercept of the two trendlines are observed (differing by 0.353), whereas the gradients are of the same magnitude. As this difference is mostly in the intercept, if the plasticiser type were identified as DINP, in advance then a correction factor could be applied to the spectroscopic data to account for this and allow accurate prediction of the plasticiser concentration.

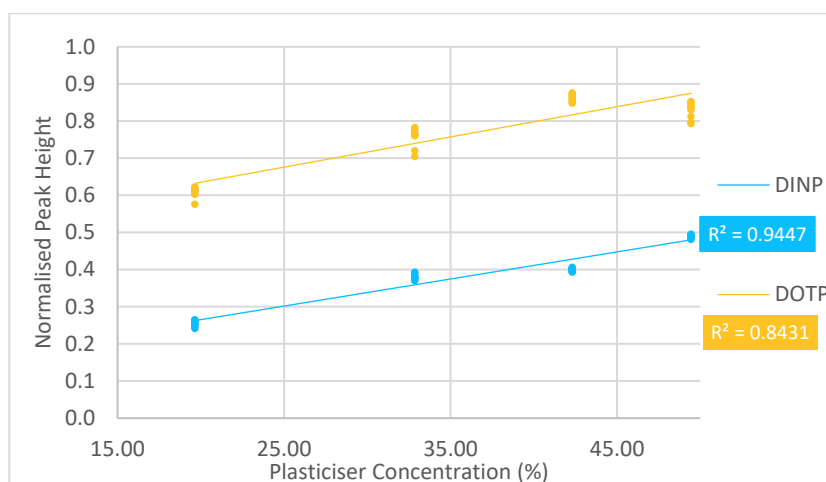


Figure 6-55: Graph of normalised peak height versus percentage plasticiser concentration.

6.4.1.2.2.2 ESBO

As with DINP, ESBO has a different chemical structure and therefore when tested using FT-IR it would be expected that differences would occur. Therefore, the effectiveness of the FTIR-fitting software needed to be assessed to investigate whether the fitting software could still be used to determine the plasticiser concentration within the pPVC.

Figure 6-56 gives the plasticiser concentration versus the normalised peak height for formulations made with both DOTP plasticiser and DOTP plasticiser with 5 PHR being replaced with ESBO plasticiser. Both DOTP and DOTP with ESBO give a correlation, with an R^2 value of 0.7436 and 0.7648, respectively. The trendlines show different gradients and intercepts, when looking at the distribution of the data on the graphs there are variations in the pattern of the data. The data was therefore separated into filled and unfilled formulations to determine whether this was having a significant influence on the data.

Figure 6-57 shows the plasticiser concentration versus the normalised peak height for the DOTP and DOTP with ESBO in filled PVC formulations. Both DOTP and DOTP with ESBO gave very strong correlations, with R^2 values of 0.9819 and 0.9650, respectively. The values found when only using DOTP are consistently higher than those found when using 5 PHR of ESBO, though the difference between the trendlines is small. The gradients, however, are of similar magnitude.

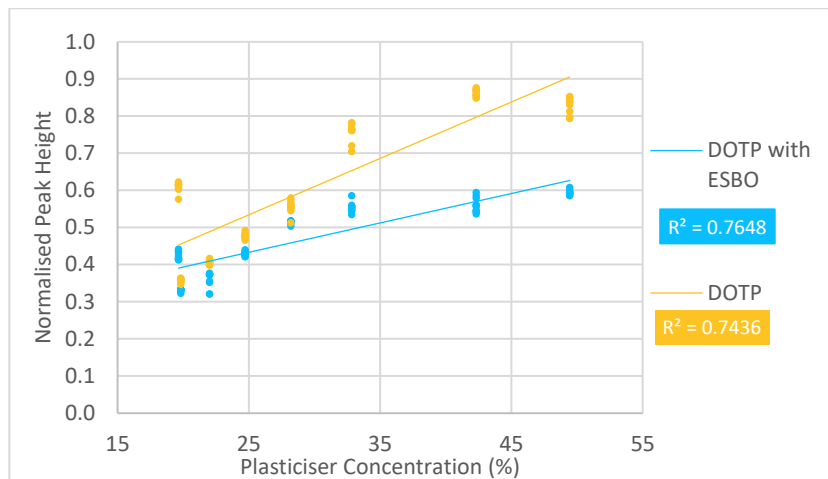


Figure 6-56: Graph showing the normalised peak height plotted against plasticiser concentration in DOTP based PVC compound with and without ESBO.

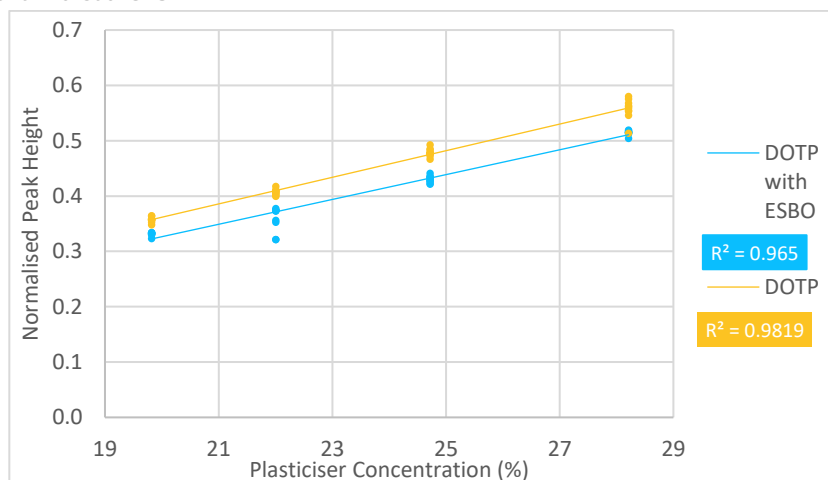


Figure 6-57: Graph showing the normalised peak height plotted against plasticiser concentration in filled DOTP based PVC compound with and without ESBO.

Figure 6-58 gives the plasticiser concentration versus the normalised peak height for the DOTP and DOTP with ESBO in unfilled PVC formulations. Both gave strong correlations with R^2 values of 0.8431 (DOTP) and 0.8449 (DOTP with ESBO). A larger difference can be seen between the DOTP and DOTP with ESBO with the unfilled samples when compared with the filled samples. Whilst the gradients are of similar magnitude, there is a significant difference in the intercept.

The results found for Figure 6-57 and Figure 6-58 suggest that if the presence of ESBO plasticiser is identified in advance then an adjustment factor could be used in order to determine the overall plasticiser concentration.

Figure 6-59 shows the plasticiser concentration versus the normalised peak height for four formulations (combinations of ESBO and DOTP) containing 50 PHR plasticiser overall. A

strong correlation is found, with an R^2 value of 0.9768. With an increase in the ESBO concentration, a decrease in the normalised peak area can be observed. This suggests that ESBO plasticiser gives a lower peak height than the DOTP, when ESBO is used on its own, a satisfactory peak height is identified.

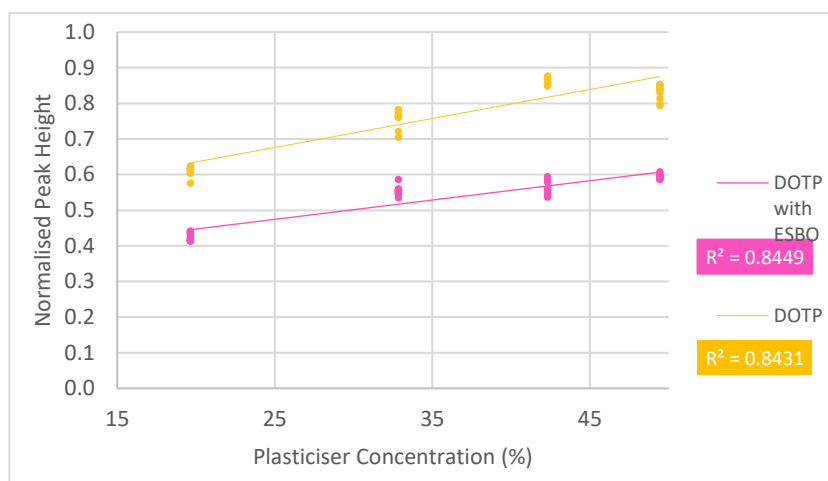


Figure 6-58: Graph showing the normalised peak height plotted against plasticiser concentration in unfilled DOTP based PVC compound with and without ESBO.

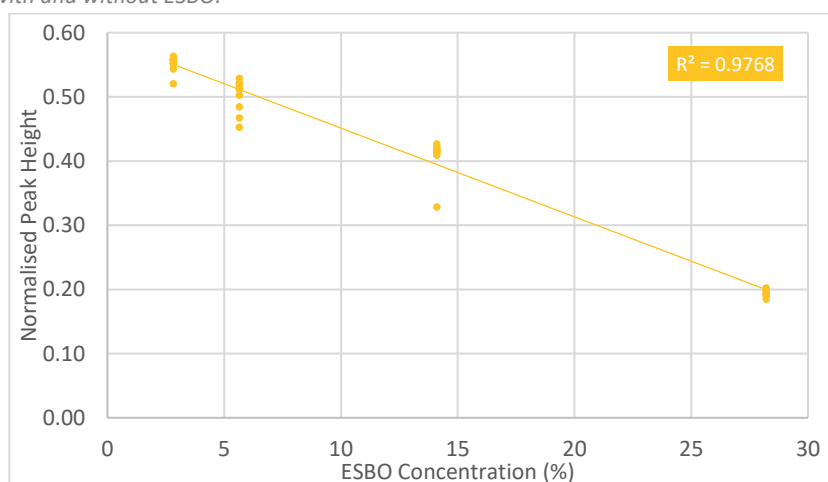


Figure 6-59: Graph of normalised peak height versus ESBO concentration in percentage (as a replacement for the DOTP at a 1:1 ratio) in PVC compound.

6.4.1.2.3 Filler Variations

The influence of the filler type on the FT-IR spectroscopy was investigated. The filler used within this study are calcium carbonate that have all been processed differently and from different sources, these differences could affect the spectroscopic results.

Figure 6-60 shows the normalised peak height for four different calcium carbonate types within an otherwise identical formulation. The lowest value found is for the industrial grade calcium carbonate with the highest value being found being for coated GCC. The

difference in these values suggests that further investigation is required into the influence of the calcium carbonate type on the spectroscopic analysis. These differences could be due to the composition of the calcium carbonate, determined by the locations of the calcium carbonate source and whether it is from chalk, limestone, or marble.

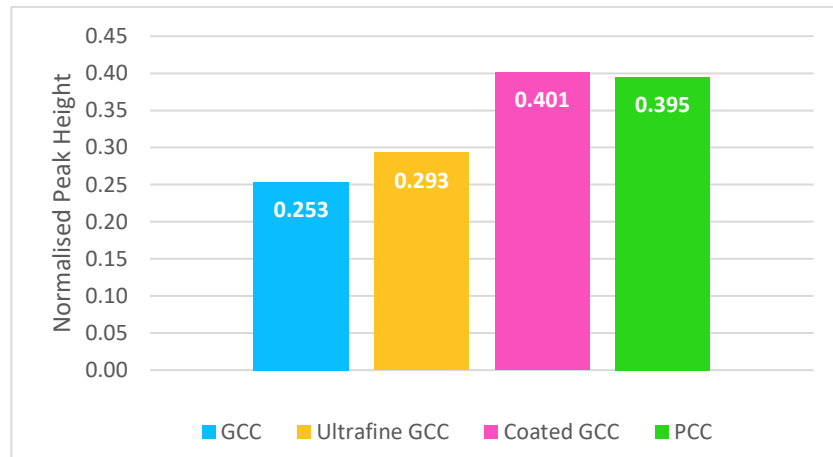


Figure 6-60: Graph showing the differences in normalise peak height for different types of calcium carbonate filler.

Figure 6-61 shows the calcium carbonate concentration versus the normalised peak height for both GCC and PCC. Both calcium carbonates gave strong correlations., with the gradient and intercept differing between the two trendlines. This makes it more difficult to easily adjust the values, if there was an indication that a different filler was being used there is the potential that an adjustment factor could be used to account for this within a model.

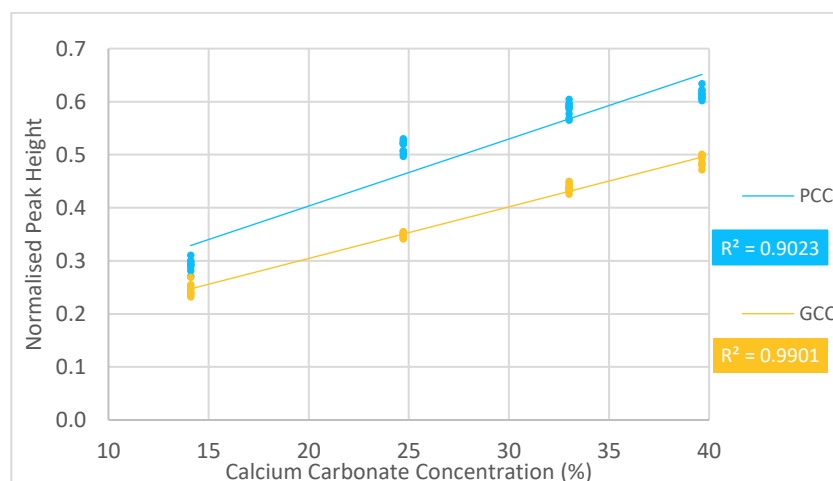


Figure 6-61: Graph showing the difference in normalised peak height between GCC and PCC filler.

6.4.1.2.4 Stabiliser Pack Variations

Figure 6-62 gives the correlation between the stabiliser package concentration versus the normalised peak height for the stabiliser package. Despite the increase in the stabiliser package present no correlation can be seen between the stabiliser package concentration and the normalised peak area. This further confirms what has previously been observed that the spectroscopic data cannot be used for the prediction of the stabiliser package concentration.

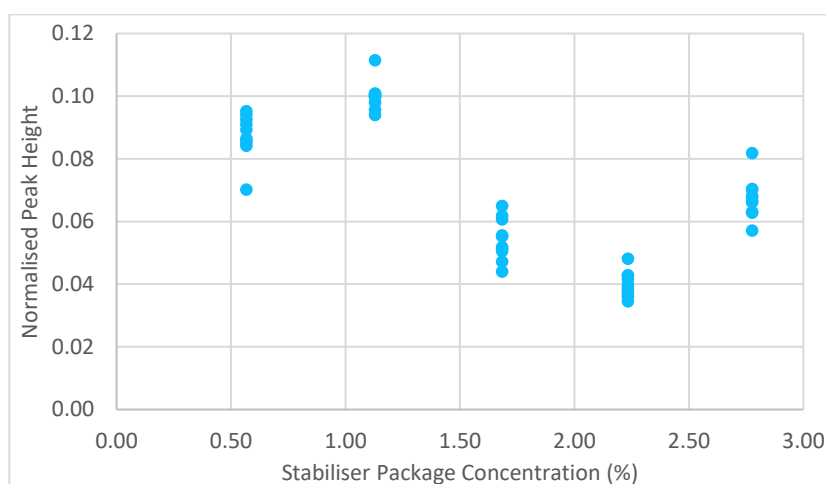


Figure 6-62: Graph showing the normalised peak height versus percentage stabiliser package concentration.

6.4.1.3 FT-IR Spectroscopy Conclusions

The results found from the FT-IR spectroscopy analysis shows that strong correlations exist between PVC resin, plasticiser and calcium carbonate, and their respective peak heights. However, this is not the case for the stabiliser package. The phase 3 results, in which alterations were made to the raw material types, demonstrates that strong correlations are still found for the PVC resin, plasticiser and filler, however these are not in line with those found when using the base materials used in phases 1 and 2. Therefore this needs to be considered for the creation of a predictive model.

6.4.2 Chapter 6 Conclusions

This chapter has provided sufficient evidence of relationships between both the raw material concentration and the industrial testing as well as the raw material concentrations

and the spectroscopic data. However, a solution is needed to allow the stabiliser package concentration to be predicted in lieu of accurate spectroscopic data.

The phase 3 data have proven a useful tool to determine the limitations of spectroscopic analysis, with clear differences being seen in the values obtained for different PVC resins, plasticisers, and fillers. With further work, all of these could be incorporated into a model with the use of an adjustment factor.

The following chapter will expand upon the relationships found here to create and test a predictive model for the prediction of PVC formulations and properties.

Chapter 7 follows next and describes the creation and testing of the POLEMER model.

7. POLEMERS – the Predictive Model and Phase 4 Testing

The work completed in chapters 5 and 6 allowed the creation of POLEMERS (**P**roperty and **f**ormulation predictiv**E** **M**odel for the polym**E**r indust**R**y using **S**pectroscopy). The model allows for fast evaluation of pPVC samples, the prediction of the PVC formulation from FT-IR spectra and the prediction of the material's properties from the PVC formulation.

The following chapter provides a guide to the creation of this model and its two parts. Part 1 produces predictions of raw material concentration from spectroscopic data. Part 2 predicts the tested properties – BSS, relative density, Congo red heat stability and the tensile properties from the raw materials.

As discussed in detail in Chapter 6, accurate spectroscopic data can be obtained using deconvolution software. In this project the software used was FTIR-fitting. The model is based on the results from FTIR-fitting, for the prediction of the raw materials present in a sample. There is no reason that other deconvolution software or automatic integration software cannot be used providing that the user is satisfied that the results obtained are correctly and accurately providing the percentages of the raw materials present and the predicted raw material levels can be inputted into the second part of the model.

FT-IR was used to model the PVC formulations, since the results tested in Chapter 5 showed that FT-IR spectroscopy was more robust than Raman spectroscopy. This decision was made because much better correlations were observed between raw materials and the properties of PVC compound and FTIR instruments are cheaper and more widely available within the PVC industry.

POLEMERS – The predictive model can be accessed in the following folder:

[POLEMERS](#)

7.1 Overview of the Model

This section provides a guide to each section of the model itself. Explaining where data can be input and what data can be expected with the output. It also covers the use of the option buttons within the model that allow the user to refine the model to their use. A “How To” guide can also be found within the model itself under the tab “How To”.

7.1.1 Basic Information

The model was created using Microsoft Excel. Whilst there are many different software options that could have been chosen, Microsoft Excel has the simple advantage that it is already present on most computers around the world and most PC users have a basic knowledge of how to use it. This means that the model is accessible to anyone within the PVC compounding industry, or within academia, intending to use it.

7.1.2 Using the Model

To explain how to use the model, a screenshot was taken and annotated (Figure 7-1), each of the numbered annotations corresponds to a point on the following list that outlines the purpose of that section within the model and clearly states whether data can be inputted by the user within this section.

1. Input

Section 1 gives the option between using the FT-IR data or using a specific BOM. The only input type allowed here is the selection of the relevant option button.

2. Formulation Type

Section 2 gives the option to select either a filled or unfilled material. This can be determined by the presence of a filler peak within the FT-IR or in some cases by the appearance of the material itself. When using a predetermined BOM this will set to be “unfilled” only when there is no filler present within said BOM. The only input type allowed here is the selection of the relevant option button.

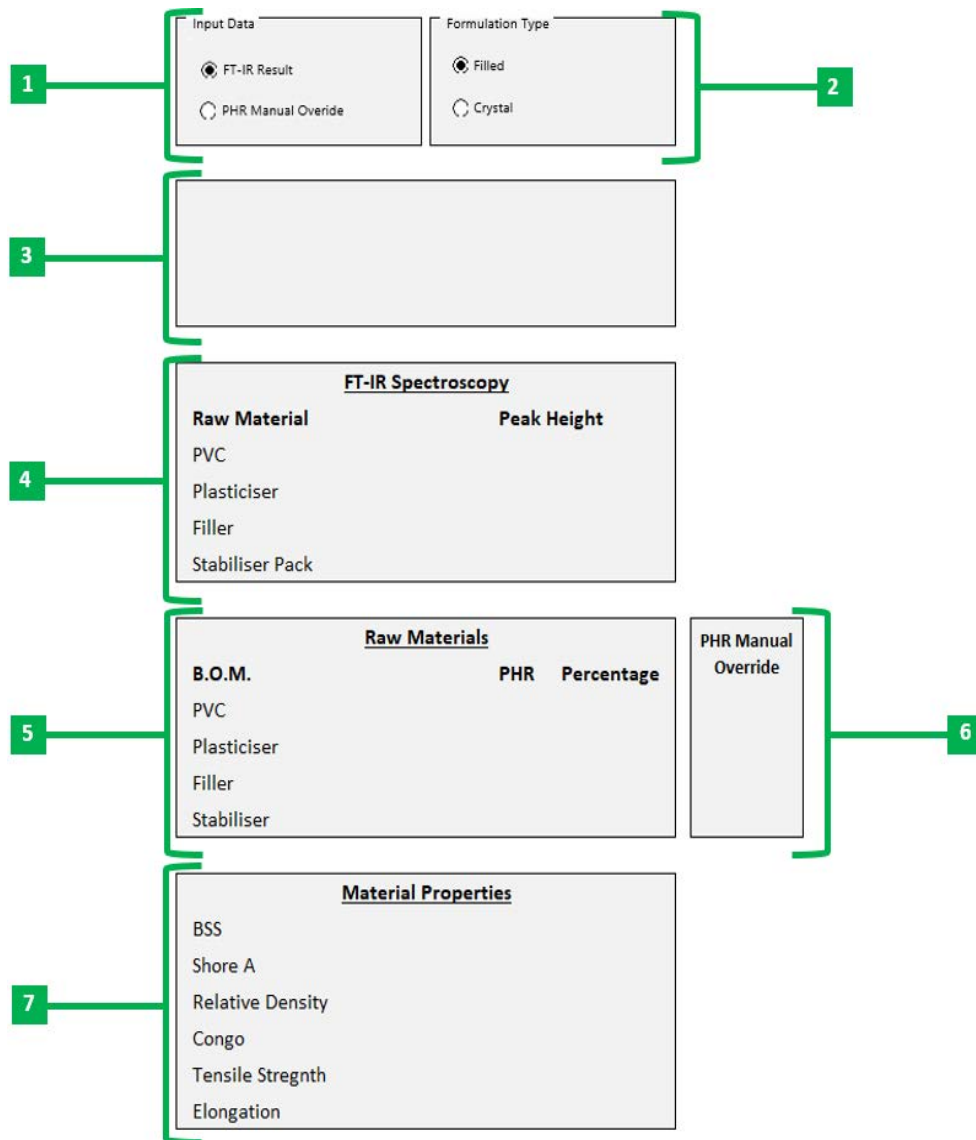


Figure 7-1: Screen shot of POLEMER with each section numbered corresponding to the descriptions below.

3. Warnings

This section gives any relevant warnings regarding the material, when applicable the warnings will appear as seen in the box as demonstrated in Figure 7-2. Table 7-1 shows all the potential warnings that can be triggered, along with their triggers and their purpose within the model. This section is output only, and no data input is possible.

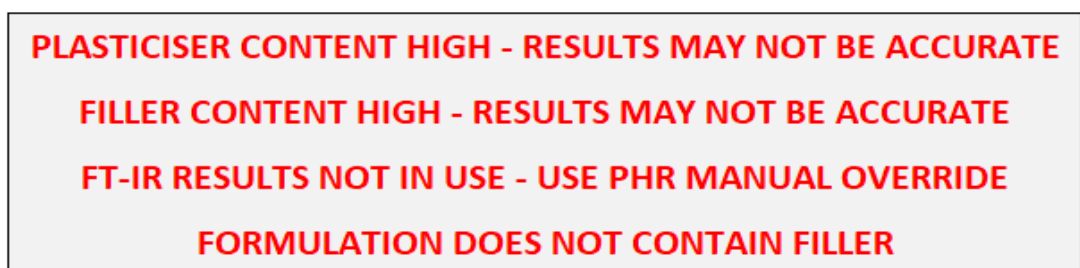


Figure 7-2: Image showing the warning box from the model, demonstrating four warnings that can be triggered.

Table 7-1: Table of each of the potential warnings that can be applicable, their triggers and the purpose of the warning.

Warning	Trigger	Purpose
Plasticiser content low – results may not be accurate.	Plasticiser level is less than 20 PHR.	To warn the user that at this level the result may not be as accurate.
Plasticiser content high – results may not be accurate.	Plasticiser level is greater than 80 PHR.	To warn the user that at this level the result may not be as accurate.
Filler content low – results may not be accurate.	Filler level is less than 20 PHR.	To warn the user that at this level the result may not be as accurate.
Filler content high – results may not be accurate.	Filler level is greater than 80 PHR.	To warn the user that at this level the result may not be as accurate.
FT-IR results not in use – use manual override.	PHR manual override option button is selected in “Input Data”.	To ensure the user is aware they are using the PHR manual override.
Formulation does not contain filler.	Unfilled option button in selected in “Formulation Type”.	To ensure that the user is aware that they are using the correct calculation.

4. FT-IR Spectroscopy

Section 4 allows for data output from FTIR-fitting to be inputted following the deconvolution using appropriate software. For this section to be active the option button for FT-IR Spectroscopy in “Input Data” needs to be selected, in section 1.

5. Raw Materials

Section 5 gives the predicted formulation based on the input provided. The raw materials are presented as raw material groups (PVC Resin, Plasticiser, Filler, and Stabiliser Pack).

6. PHR Manual Override

Section 6 allows the user to input a specific BOM without using FT-IR data. For this section to be active the option button for PHR manual override in section 1 needs to be selected. This section is output only, and no data input can occur.

7. Material Properties

Section 7 displays the properties of the material as predicted from section 5. The properties given are the BSS, Shore A hardness, Relative Density, Tensile Strength, and Elongation. This section is output only, and no data input can occur.

7.2 Predictive Model Creation

To create the predictive model, it was split into two defined parts. For the creation of both parts of the model the 80% of the data collected in Phases 1 and 2 was used as the training dataset, with 20% of the data being held back as test data.

Part 1 was created to predict the PVC BOM from the fitted FT-IR data. This was completed by plotting the fitted FT-IR data (x axis) versus the raw material concentrations (y axis). The trendline found was then used within the model to allow the prediction of the raw material concentrations from the fitted FT-IR data.

Part 2 was created to predict the formulation properties from the plasticiser and filler concentrations within the compound. Both these can be varied independently, with the ratio between the PVC resin and the stabiliser package being the only constant required. This was completed by plotting the raw material concentrations (x axis) versus the property being predicted (y axis). The trendline found was then used within the model to allow the prediction of the properties from the raw material concentrations.

All equations used within the model were to 10 decimal places as it was found that until this point that a significant impact on the predictions occurred.

7.1.1 Model Part 1 – Bill of Materials Prediction via FT-IR Spectroscopy

In this section the equations used for the first iteration of the model were established from the graphs of the normalised fitted peak data versus the raw material concentrations. This was split into two sections, filled PVC and unfilled PVC.

7.2.1.1 Filled PVC

The normalised FT-IR peak data for the filled PVC samples were plotted against the raw material concentrations in Figure 7-3 with the trendlines added. The equation used for the prediction of each raw material from the normalised fitted peak data are pulled from the trendlines displayed on the graphs. The equation for each raw material is in Table 7-2.

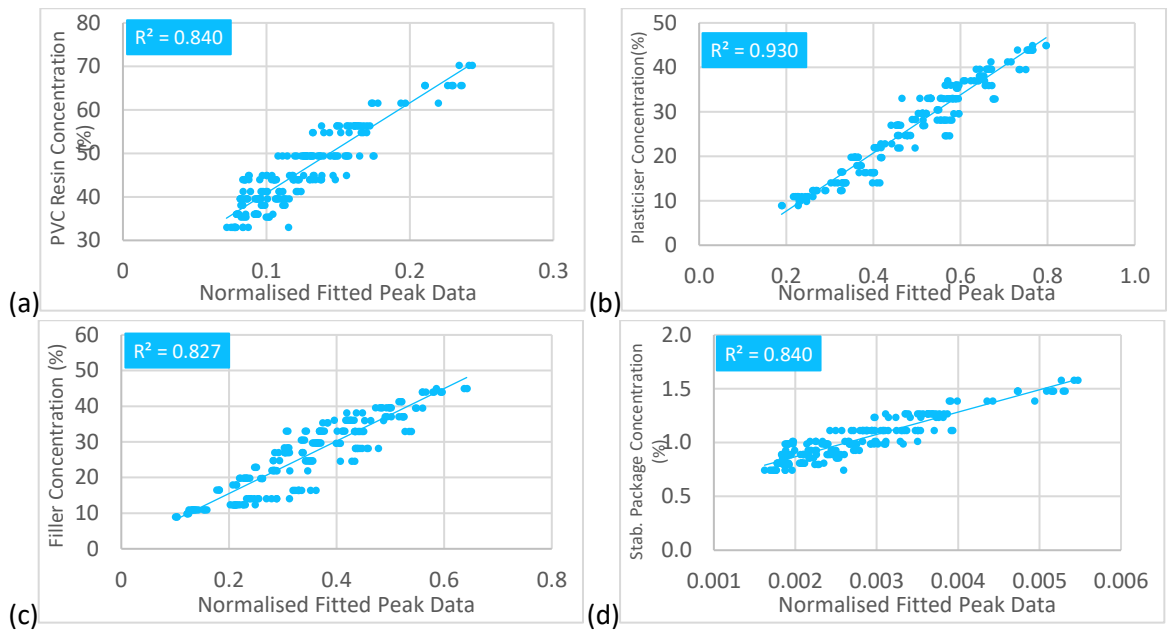


Figure 7-3: Shows the raw material concentrations for the four raw materials (PVC Resin (a), Plasticiser (b), Filler (c) and stabiliser package (d)) over the normalised fitted peak data from the FTIR-fitting software, for filled pPVC.

Table 7-2: Table giving the line equations, for each raw material, for the first iteration of the model along with their R^2 values, for filled pPVC.

Raw Material	Line Equation	R^2 Value
PVC Resin	$y = 207.502x + 20.130$	0.840
Plasticiser	$y = 65.403x - 5.412$	0.930
Filler	$y = 73.671x + 0.758$	0.827
Stabiliser Package	$y = 207.506x + 0.453$	0.840

7.2.1.2 Unfilled PVC

The normalised FT-IR peak data, for the unfilled samples, was plotted against the raw material concentration in Figure 7-4 with trendlines added.

The equation used for the prediction of each raw material from the fitted peak data are directly from the trendlines displayed on the graphs. The equation for each raw material is given in Table 7-3.

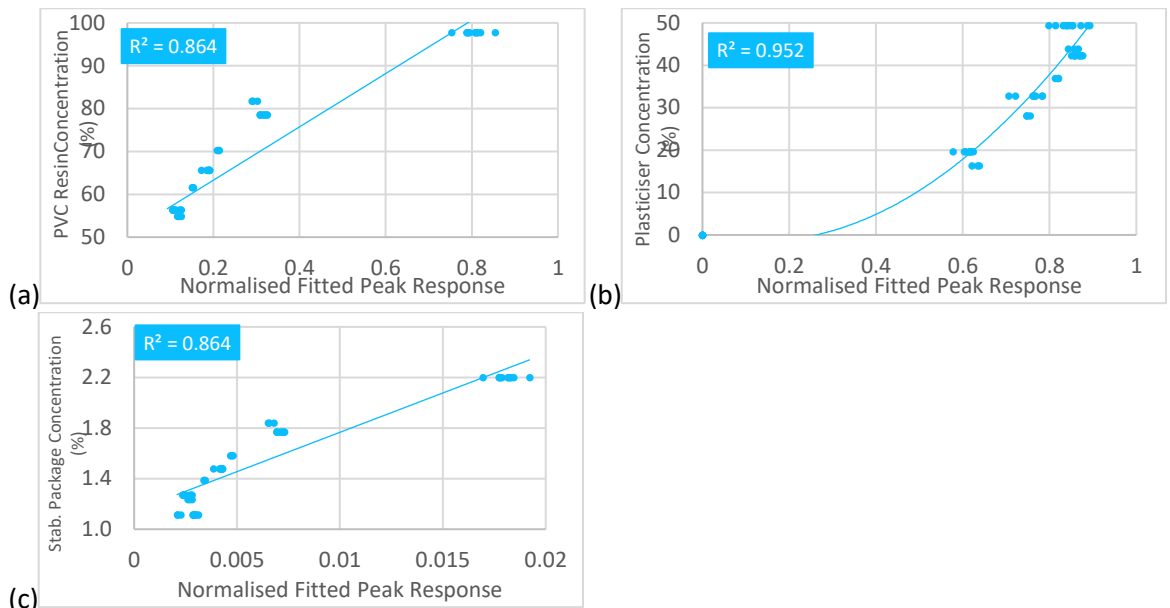


Figure 7-4: Shows the raw material concentrations for the three raw materials (PVC Resin (a), Plasticiser (b), and stabiliser package (c)) over the normalised fitted peak data from the FTIR-fitting software, for unfilled pPVC.

Table 7-3: Table giving the line equations, for each raw material, for the first iteration of the model along with their R^2 values, for unfilled pPVC.

Raw Material	Line Equation	R^2 Value
PVC Resin	$y = 62.190x + 50.865$	0.864
Plasticiser	$y = 87.941x^2 - 22.973x - 0.0103$	0.952
Stabiliser Package	$y = 62.189x + 1.144$	0.864

7.2.2 Model Part 2 – Property Prediction from Bill of Materials

In this section the equations used for the first iteration of the model were established from the graphs of the of the actual material properties versus the predicted material properties.

This was split into two sections, filled PVC and unfilled PVC.

7.2.2.1 Filled PVC

Raw material concentrations for the filled PVC samples were plotted against properties: BSS, relative density, Congo red heat stability, tensile strength, and elongation at yield.

7.2.2.1.1 British Standard Softness

For BSS, the plasticiser concentration was plotted versus the BSS, with the data being divided by the filler concentration (in PHR) (Figure 7-5 (a)). The line equations and R^2 values for each filler concentration being listed in Table 7-4, with the gradients and intercepts being listed separately. Figure 7-5 (b) gives the filler concentration, in PHR, versus the

gradient (blue) and the intercept (yellow) from Table 7-4. Strong correlations can be observed for both, with R² values of 0.9935 and 0.9474, respectively.

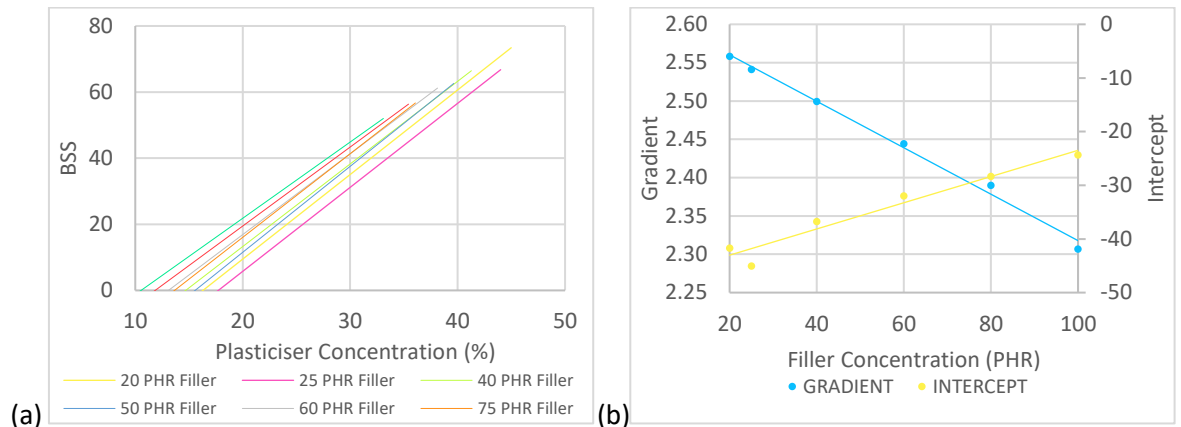


Figure 7-5: Graph (a) showing the plasticiser concentration versus the BSS, subdivided by the filler concentration in PHR, with only the trendlines being displayed, and graph (b) showing the filler concentration versus both the gradient and intercept identified in graph (a), with a linear trendline added for both variables.

Table 7-4: Table of the line equations, for each filler concentration, along with their R² values, for unfilled pPVC.

Filler Concentration (PHR)	Line Equation	Gradient	Intercept	R ² Value
20	$y = 2.558x - 41.688$	2.558	-41.688	0.958
25	$y = 2.541x - 45.053$	2.541	-45.053	0.959
40	$y = 2.499x - 36.718$	2.499	-36.718	0.953
50	$y = 2.601x - 40.486$	2.601	-40.486	0.952
60	$y = 2.444x - 31.995$	2.444	-31.995	0.951
75	$y = 2.530x - 34.537$	2.530	-34.537	0.949
80	$y = 2.390x - 28.318$	2.390	-28.318	0.960
100	$y = 2.307x - 24.308$	2.307	-24.308	0.949

Using the information established from Figure 7-5 the following equation was produced to predict the BSS of a given BOM. The equation uses the relationship found from Figure 7-5 (b) to give the predicted gradient (blue) and intercept (yellow) at a given filler level in PHR.

With x being the plasticiser concentration in percentage.

BSS:
$$y = (-0.003a + 2.621)x + (0.244a - 47.909)$$

Where: $a = \text{Filler Level in PHR}$

$x = \text{Plasticiser Level in percentage}$

7.2.2.1.2 Shore A

The Shore A value was calculated from the BSS value using the equation found from the trendline in Figure 7-6, as seen below.

Shore A: $y = -0.513x + 96.946$

Where: $x = BSS$

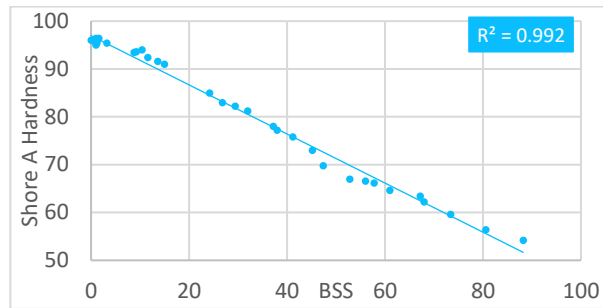


Figure 7-6: Graph of the BSS versus the Shore A hardness, showing a strong linear correlation.

7.2.2.1.3 Relative Density

The relative density was plotted against the filler concentration at intervals corresponding to the plasticiser level in PHR (Figure 7-7 (a)). The line equations, gradients, intercepts and R² values for each plasticiser concentration are listed in Table 7-5.

Figure 7-7 (b) gives the plasticiser concentration, in PHR, versus the gradient (blue) and the intercept (yellow) from Table 7-5. Strong correlations can be observed between PHR filler and both gradient and intercept, with R² values of 0.8827 and 0.9917, respectively.

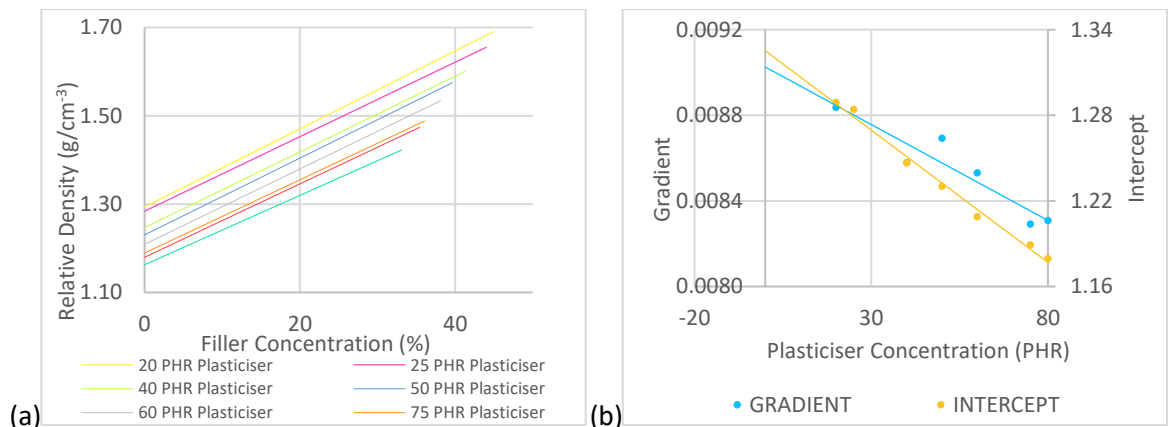


Figure 7-7: Graph (a) showing the filler concentration in percentage versus the relative density, subdivided by the plasticiser concentration in PHR, with the trendlines being displayed, and graph (b) showing the plasticiser concentration versus both the gradient and intercept identified in graph (a), with a linear trendline added for both variables.

Table 7-5: Table of the line equations, for each subdivided plasticiser concentration, with their R² values, for unfilled pPVC.

Plasticiser Concentration (PHR)	Line Equation	Gradient	Intercept	R ² Value
20	$y = 0.00884x + 1.289$	0.00884	1.289	0.990
25	$y = 0.00843x + 1.284$	0.00843	1.284	0.975
40	$y = 0.00858x + 1.247$	0.00858	1.247	0.989
50	$y = 0.00869x + 1.230$	0.00869	1.230	0.994
60	$y = 0.00853x + 1.209$	0.00853	1.209	0.993
75	$y = 0.00829x + 1.189$	0.00829	1.189	0.995
80	$y = 0.00831x + 1.180$	0.00831	1.180	0.992
100	$y = 0.00785x + 1.163$	0.00785	1.163	0.987

Using the information established from Figure 7-7 the following equation was produced to predict the relative density of a given BOM. The equation uses the relationship found from Figure 7-7 (b) to give the predicted gradient (blue) and intercept (yellow) at a given plasticiser concentration in PHR. With x being the filler concentration in percentage.

Relative Density: $y = (-0.00001 \times a + 0.010)x + (-0.002 \times a + 1.292)$

Where:

$a = \text{Plasticiser Concentration in PHR}$

$x = \text{Filler Concentration in percentage}$

7.2.2.1.4 Congo Red Heat Stability

Figure 7-8 (a) gives the plasticiser concentration versus the Congo red heat stability at varying filler levels in PHR. The line equations, gradients, intercepts and R^2 values for each filler concentration are listed in Table 7-6. Figure 7-8 (b) gives the filler concentration versus the gradient (blue) and intercept (yellow) from Table 7-6. Strong correlations are observed, with R^2 values of 0.9278 and 0.8536, respectively.

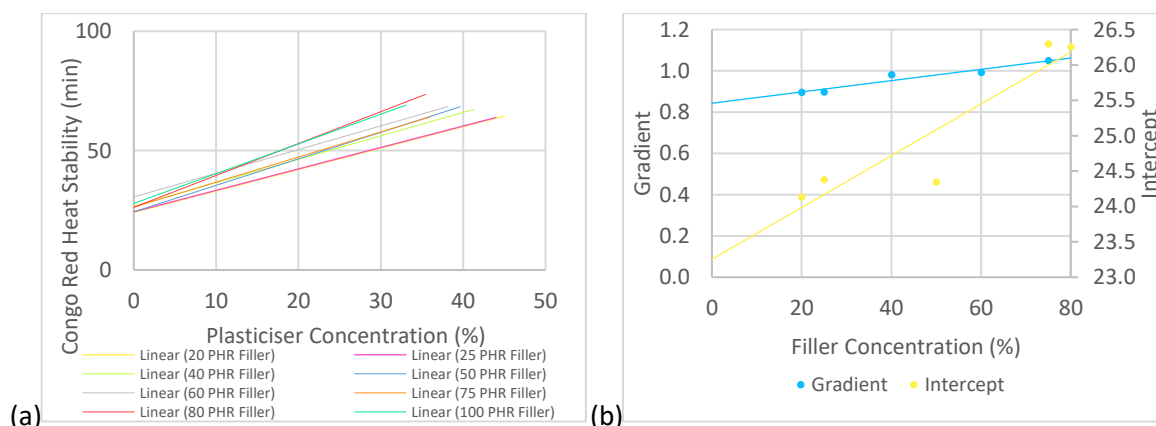


Figure 7-8: Graph (a) the plasticiser concentration versus the Congo red heat stability, subdivided by the filler concentration in PHR, graph (b) showing the filler concentration versus both the gradient and intercept identified in graph (a), with a linear trendline added for both variables

Table 7-6: Table giving the line equations, for each subdivided filler concentration, with their R^2 values, for unfilled pPVC.

Filler Concentration (PHR)	Line Equation	Gradient	Intercept	R^2 Value
20	$y = 0.896x + 24.136$	0.896	24.136	0.962
25	$y = 0.898x + 24.378$	0.898	24.378	0.910
40	$y = 0.982x + 26.744$	0.982	26.744	0.967
50	$y = 1.111x + 24.350$	1.111	24.350	0.906
60	$y = 0.992x + 30.597$	0.992	30.597	0.903
75	$y = 1.051x + 26.298$	1.051	26.298	0.832
80	$y = 1.335x + 26.225$	1.335	26.255	0.947
100	$y = 1.246x + 27.896$	1.246	27.896	0.788

Using the information established from Figure 7-8 the following equation was produced to predict the Congo red heat stability of a given BOM. The equation uses the relationship found from Figure 7-8 (b) to give the predicted gradient (blue) and intercept (yellow) at a given filler concentration in PHR. With x being the plasticiser concentration in percentage.

Congo Red Heat Stability: $y = (0.003 \times a + 0.843)x + (0.037 \times a + 23.254)$

Where:

a = Filler concentration in PHR

x = Plasticiser concentration in percentage

y = Congo red heat stability in minutes

7.2.2.1.5 Tensile Strength

The tensile strength was plotted against the raw material concentration at intervals corresponding to the filler level in PHR (Figure 7-9 (a)). The line equations, gradients, intercepts and R^2 values for each filler concentration are listed in Table 7-7. Figure 7-9 (b) gives the filler concentration, in PHR, versus the gradient (blue) and the intercept (yellow) from Table 7-7. A strong correlation can be observed for both the gradient and intercept, with R^2 values of 0.8963 and 0.9933, respectively.

Using the information established from Figure 7-9 the following equation was produced to predict the tensile strength of a given BOM. The equation uses the relationship found from Figure 7-9 (b) to give the predicted gradient (blue) and intercept (yellow) at a given filler concentration in PHR. With x being the plasticiser concentration in percentage.

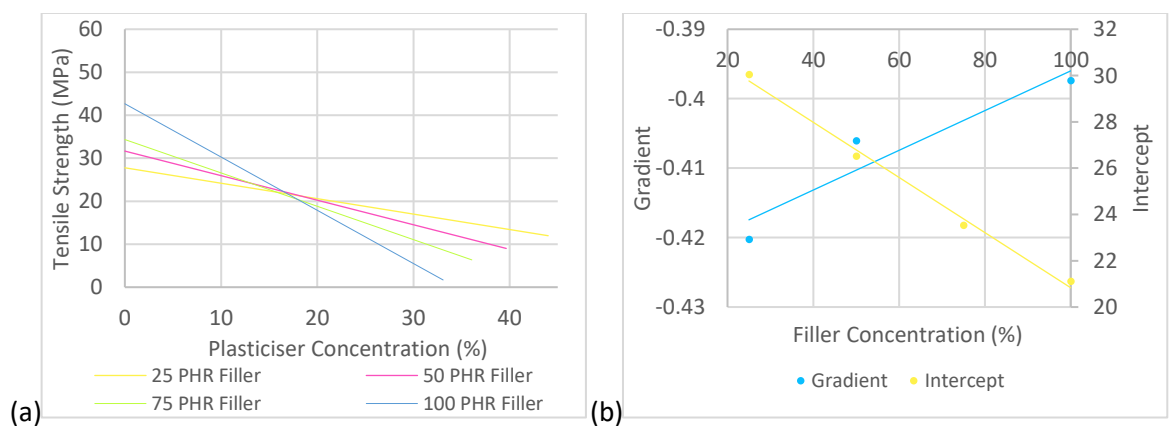


Figure 7-9: Graph (a) showing the plasticiser concentration versus the tensile strength, subdivided by the filler concentration in PHR, with only the trendlines being displayed, and graph (b) showing the filler concentration versus both the gradient and intercept identified in graph (a), with a linear trendline added for both variables.

Table 7-7: Line equations, for each subdivided filler concentration, along with their R² values, for unfilled pPVC.

Filler Concentration (PHR)	Line Equation	Gradient	Intercept	R ² Value
25	$y = -0.464x + 30.959$	-0.359	27.772	0.965
50	$y = -0.410x + 26.423$	-0.571	31.660	0.947
75	$y = -0.381x + 23.189$	-0.776	34.344	0.863
100	$y = -0.400x + 21.190$	-1.239	42.669	0.757

Tensile Strength: $y = (-0.011 \times a - 0.025)x + (0.190 \times a + 22.268)$

Where: $a = \text{Filler Level in PHR}$

$x = \text{Plasticiser Level in percentage}$

7.2.2.1.6 Elongation

Figure 7-10 (a) gives the plasticiser concentration versus the tensile strength at intervals corresponding to the filler level in PHR. The line equations and R² values for each filler concentration are listed in Table 7-8 with the gradients and intercepts being listed separately. Figure 7-10 (b) gives the filler concentration, in PHR, versus the gradient (blue) and the intercept (yellow) from Table 7-8. A very strong correlation can be observed for both the gradient and the intercept, with R² values of 0.9929 and 0.9764, respectively.

Using the information established from Figure 7-10 the following equation was produced to predict the elongation of a given BOM. The equation uses the relationship found from Figure 7-10 (b) to give the predicted gradient (blue) and intercept (yellow) at a given filler concentration in PHR. With x being the plasticiser concentration in percentage.

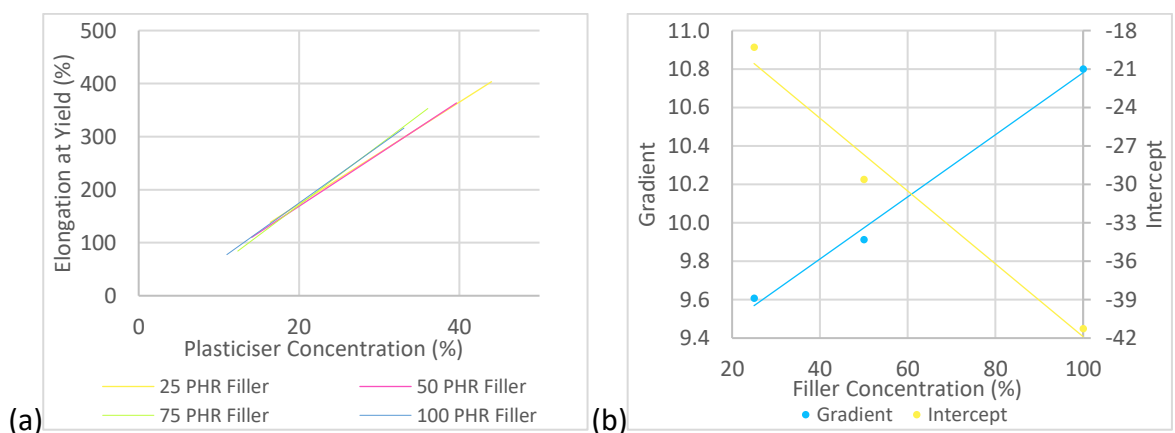


Figure 7-10: Graph (a) showing the plasticiser concentration versus the elongation at yield, subdivided by the filler concentration in PHR, with only the trendlines being displayed, and graph (b) showing the filler concentration versus both the gradient and intercept identified in graph (a), with a linear trendline added for both variables.

Table 7-8: Line equations, for each subdivided filler concentration, along with their R² values, for unfilled pPVC.

Filler Concentration (PHR)	Line Equation	Gradient	Intercept	R2 Value
25	$y = 9.608x - 19.296$	9.608	- 19.296	0.930
50	$y = 9.915x - 26.674$	9.915	- 26.674	0.989
75	$y = 11.433x - 60.653$	11.433	- 60.653	0.939
100	$y = 11.078x - 46.214$	11.078	- 46.214	0.995

Elongation at Yield: $y = (0.016 \times a + 9.165)x + (-0.284 \times a - 13.466)$

Where:

$a = \text{Filler Level in PHR}$

$x = \text{Plasticiser Level in percentage}$

7.2.2.2 Unfilled PVC

The plasticiser concentrations for the unfilled PVC samples were plotted against the properties; BSS, relative density, Congo red heat stability, tensile strength, and elongation at yield to determine the trendline and therefore the trendline equations (Figure 7-11). Strong correlations were found for each property; BSS, relative density, Congo red heat stability, tensile strength, and elongation, with R² values of 0.9699, 0.9789, 0.8600, 0.9070 and 0.8402, respectively. With the equations given in Table 7-9.

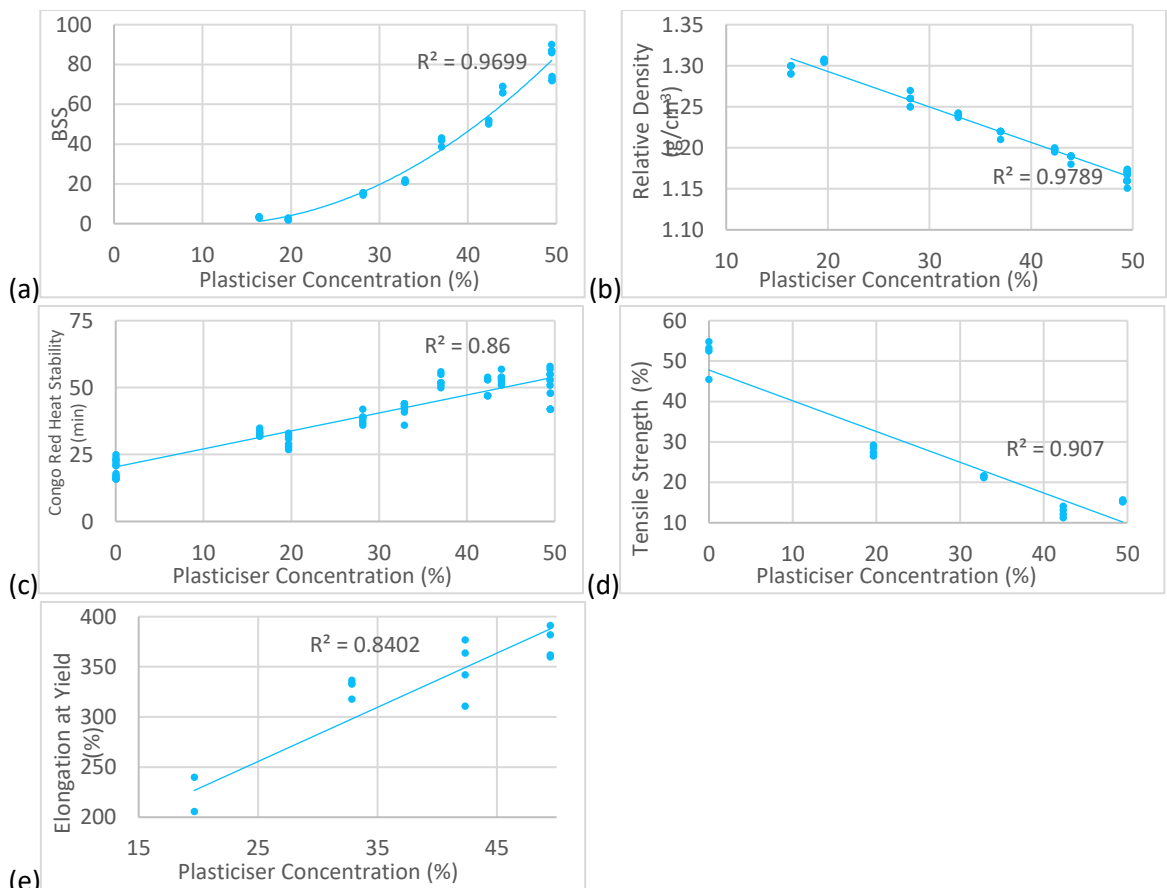


Figure 7-11: Shows the graphs of plasticiser concentration in the tests completed (BSS (a), Relative Density (b), Congo Red Heat Stability (c), Tensile Strength (d), and Elongation at yield (e)), for the Phase 1 & 2 unfilled samples.

Table 7-9: Table giving the line equations, for each material property, for the first iteration of the model along with their R² values, for unfilled pPVC.

Property	Line Equation	R ² Value
BSS	$y = 0.056x^2 - 1.230x + 6.349$	0.970
Relative Density	$y = -0.004x + 1.379$	0.979
Congo Red Heat Stability	$y = 0.671x + 20.400$	0.860
Tensile Strength	$y = -0.760x + 47.782$	0.907
Elongation	$y = 7.324x + 44.599$	0.936

7.3 Testing of the Model

In this section the model was tested. Initially the testing was completed against the phase 1 and 2 data, after which corrections were made to the model and testing was completed against the Phase 4 data.

7.3.1 Phase 1 and 2 Test Data

In this section the remaining 20% of Phase 1 and 2 data not used in the creation of the model was used to test the model.

7.3.1.1 FT-IR Spectroscopy

To assess the success of the first part of the model both graphs of the correlation between the actual and predicted concentrations and residual plots were produced for the four raw materials used (PVC resin, plasticiser, filler, and the stabiliser package). The graphs produced can be seen in Figure 7-12. Figure 7-12 gives the correlation between the actual raw material levels, the predicted raw material levels from the model, as well as the residual plot for each raw material. The residual plots all have a red line on the x axis indicating the zero and therefore the line between positive and negative values. Strong linear correlations were found between the predicted and actual raw material levels, demonstrating that the model is valid, with some variation. High R² values being found for each confirm these correlations. Residual plots were created to find what the spread of the data was, and the residual plots shown in the figure all give results that are around zero, however different patterns can be observed for these raw materials. The residual

plots shown for Figure 7-12 (a) and Figure 7-12 (d) demonstrate the residuals are positive and negative, however as the predicted raw material concentration increases the values tend to fall above the line, suggesting that there is bias in the data, potentially caused by the effect of an additional variable, such as the concentration of the other raw materials. The blue line signifies the trendline for the datapoints in the plots, this shows an upwards trend, suggest that as the predicted PVC resin concentration increases so does the difference between the predicted and actual PVC resin concentration. The residuals shown for Figure 7-12 (b) show the data is mostly evenly spread around the zero line, the outliers seen between 35 – 45% are the samples that contain no filler, suggesting the calculation used when no filler is present may require a correction factor in order to obtain more accurate predictions. The trendline shows that the data falls mostly on the zero, with a slight downward trend. The residual plot for filler (Figure 7-12 (c)) shows that the data is, evenly distributed both sides of the axis. However, the data becomes more widely spread as the predicted filler level increases. The data is unbiased but shows heteroscedasticity, which could indicate that there are additional variables influencing the data.

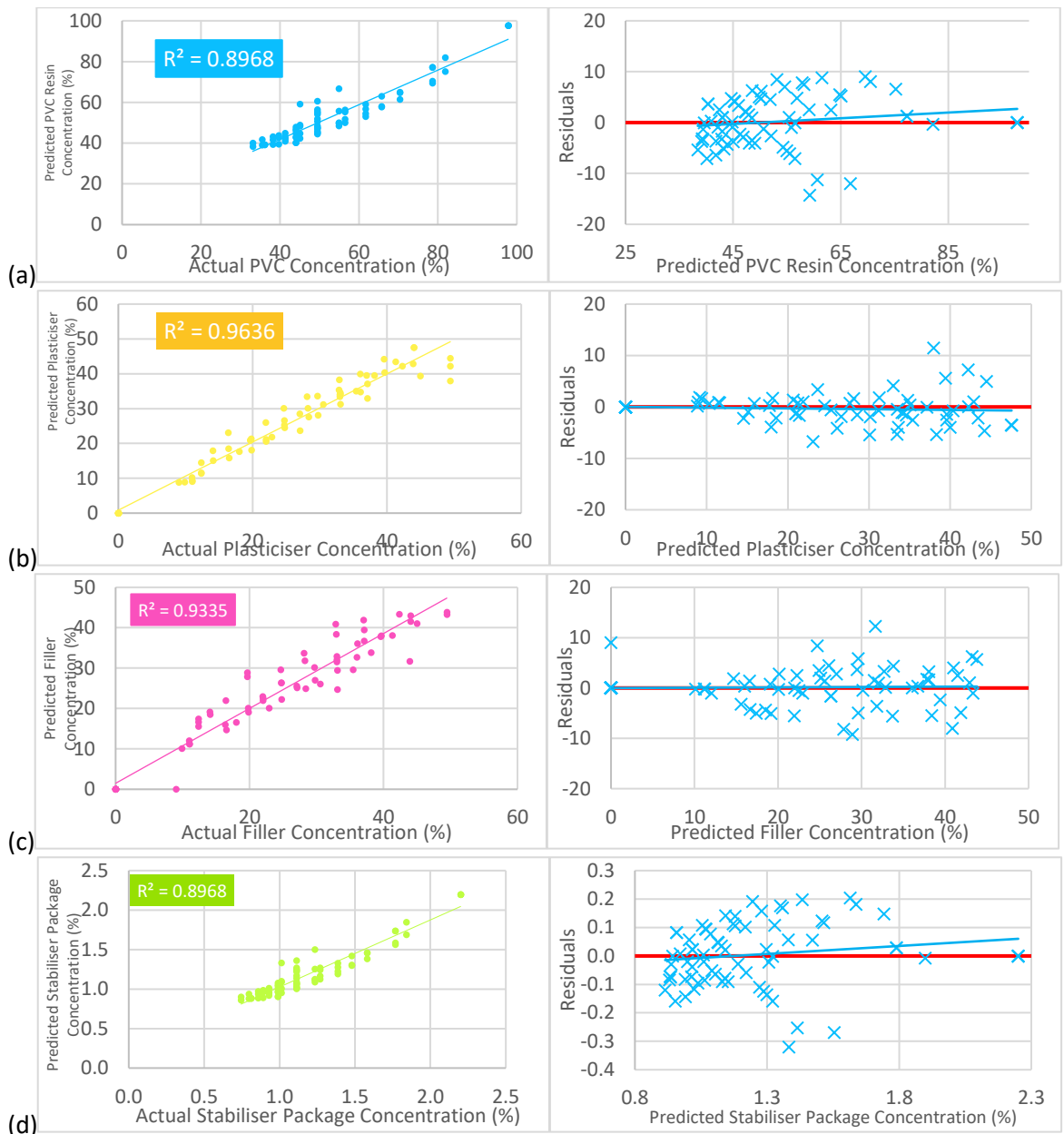


Figure 7-12: Graphs for the actual concentrations versus the predicted concentrations, and the residual plot for the predicted concentration for each raw material (PVC Resin (a), Plasticiser (b), Filler (c), and Stabiliser Package (d)), for the Phase 1 & 2 test data.

7.3.1.2 Industrial Testing

Part 2 of the model was evaluated by: (a) correlating actual and predicted material properties (BSS, relative density, Congo red heat stability, tensile strength, and elongation at yield), and (b) plotting the residual between actual and predicted values (Figure 7-13). Discrepancies between the actual and predicted values were identified, and correction factors subsequently applied (Section 0).

Figure 7-13 gives the graphs showing the correlation between the actual and predicted

values for each material property test, as well as the corresponding residual plot for each of these. The residual plots all have a red line indicating zero on the y axis and therefore the line between positive and negative values. All the actual values versus predicted values show a strong linear correlation, with high R^2 values being found. Higher variation can be seen from the data plotted in Figure 7-13 (c) and (d), reflected in the R^2 values which were 0.826 and 0.791, respectively. The residual plots for each of these shows that the residuals do fall around zero, however the pattern found for each varies significantly.

The residual plot for Figure 7-13 (a), for BSS, shows most of the datapoints are over zero, suggesting that the model is underestimating the BSS. It can also be observed that as the predicted BSS increases there are a greater number of datapoints above the zero. This pattern is confirmed by the trendline seen in the residual plot, which shows a positive gradient, getting further from the 0 residual. This is also reflected in the trendline found for the actual values versus the predicted values, in which the difference between the actual and predicted values becomes more noticeable as the values increase. This is something that can be accounted for within the model using an adjustment factor as seen in section 0.

The residual plot for Figure 7-13 (b), for relative density, shows most the residuals to be negative. With further investigation the cluster between $1.15 - 1.30 \text{ gcm}^{-3}$, sitting directly on and above the line, are those found for formulations that contain no filler. This plot therefore suggests that the model is overpredicting the relative density when the PVC material is filled. The trendline for the residual plot shows a downwards trend, starting and ending beneath the zero line. This is reflected in the trendline from the actual versus predicted values, in which the line is lying consistently at higher predicted values. The relationship suggests that with a correction factor, to lower the predicted values, the model could be brought in line with the actual values, as was completed in section 0.

The residual plot for Figure 7-13 (c) shows that at lower predicted Congo red values the residuals are grouped evenly around the zero. As the predicted Congo red values increase, the residuals begin to become mostly positive, with a wider distribution. This is shown by the trendline for the residual plot, which shows an upwards trend from zero. This suggests that for high Congo red values the model is under-predicting the values, this is also seen with the trendline for the actual versus predicted values, with the difference between the actual and predicted values becoming greater as the Congo red value increases.

The residual plot for Figure 7-13 (d) shows that at lower predicted tensile strengths (0-25 MPa) the residuals are mostly negative, past this point they are mostly positive. This is further evident by the trendline for the residual plot, which shows an upwards trend through zero to +10. This same relationship can be seen when looking at the trendline for the actual versus predicted values. Upon investigation the positive values found past 25 MPa are those found of 0% plasticiser. Therefore, a correction could be made to the model to account for both the negative values when plasticiser is present and the positive values when plasticiser is not present, was completed in section 0.

The residual plot for Figure 7-13 (e) shows a trendline with a downward trajectory, most of the residuals are positive, with the most negative values being at the highest and lowest predicted elongation at yield. The trendline for the actual versus predicted values shows the predicted values are close to the expected values. A correction factor could be used within the model to account for the differences observed, as is shown in section 0.

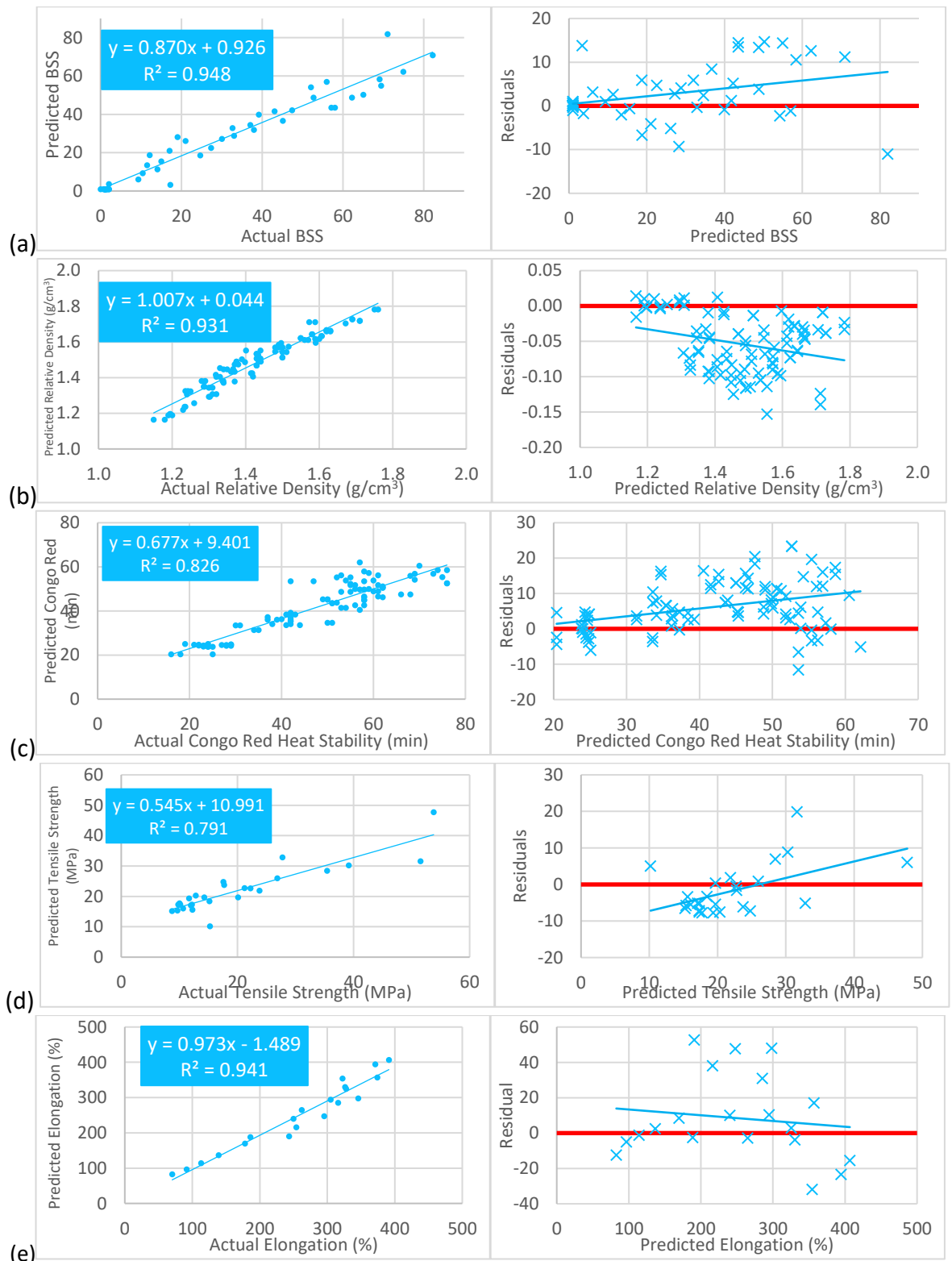


Figure 7-13: Shows the graphs for the actual values versus the predicted values, and the residual plot for the predicted values for each test completed (BSS (a), Relative Density (b), Congo Red Heat Stability (c), Tensile Strength (d), and Elongation at yield (e)), for the Phase 1 & 2 test data.

7.3.2 Phase 1 and 2 Correction

Material property measurements, carried out using standard industry techniques, identified some discrepancies between the predicted and actual values. Therefore,

correction factors were derived and applied to the model. Modelled residuals were then recalculated and are reported in this subsection.

The corrections used are outlined in the tables below: BSS - Table 7-10; Relative Density - Table 7-11; Congo red heat stability - Table 7-12; tensile strength and Table 7-13; elongation at yield - Table 7-14.

Table 7-10: Table showing the conditions and correction factors for the prediction of BSS.

Condition	Correction Factor (to Section 7.2.2.1.1)
Unfilled material	No correction required.
If BSS prediction is less than 40 BSS	$Prediction \times 1.125$
If BSS prediction is greater than 40 BSS	$Prediction \times .2 - 1$

Table 7-11: Table showing the conditions and corresponding correction factors for the prediction of relative density.

Condition	Correction Factor (to Section 7.2.2.1.3)
Unfilled material	No correction required.
If BSS prediction is less than 40 BSS	$Prediction \times 0.96$

Table 7-12: Table showing the conditions and corresponding correction factors for the prediction of Congo red.

Condition	Correction Factor (to Section 07.2.2.1.1)
Unfilled material	$Prediction \times 0.9$
If DOTP concentration greater than 10	$Prediction \times 1.30$

Table 7-13: Table showing the conditions and corresponding correction factors for the prediction of tensile strength.

Condition	Correction Factor (to 7.2.2.1.5)
Unfilled material	No correction required.
If tensile strength prediction is less than 25 MPa	$Prediction \times 0.78$
If tensile strength prediction is greater than 25 MPa	$Prediction \times 1.5 + 1$

Table 7-14: Table showing the conditions and corresponding correction factors for the prediction of elongation at yield.

Condition	Correction Factor (to Section 0)
Unfilled material	$Prediction \times 0.95$
If elongation prediction is less than 320 MPa	$Prediction \times 0.97$
If elongation prediction is greater than 320 MPa	$Prediction \times 1.05$

Figure 7-14 shows the residual plots for the original model (blue) and the corrected model (yellow) for each industrial test. Trendlines have been added for each set of data. As can be seen for each test, the datapoints are now closer to the zero line and the data is overall less spread. This is further indicated by the trendlines presented, in each case the trendlines have flattened and are sitting much closer to zero. Therefore, the corrections completed here will be used for further testing using the predictive model.

In addition to the residual plots, the root-mean-squared values were calculated before and after the corrections to ensure that were in fact improving the results.

Table 7-15 gives the RMS values both before and after the model corrections, including the percentage differences for each correction. All the RMS values decreased by a minimum of 20%, demonstrating that the correction factors have successfully altered the data to improve the model's predictions, based on the test data.

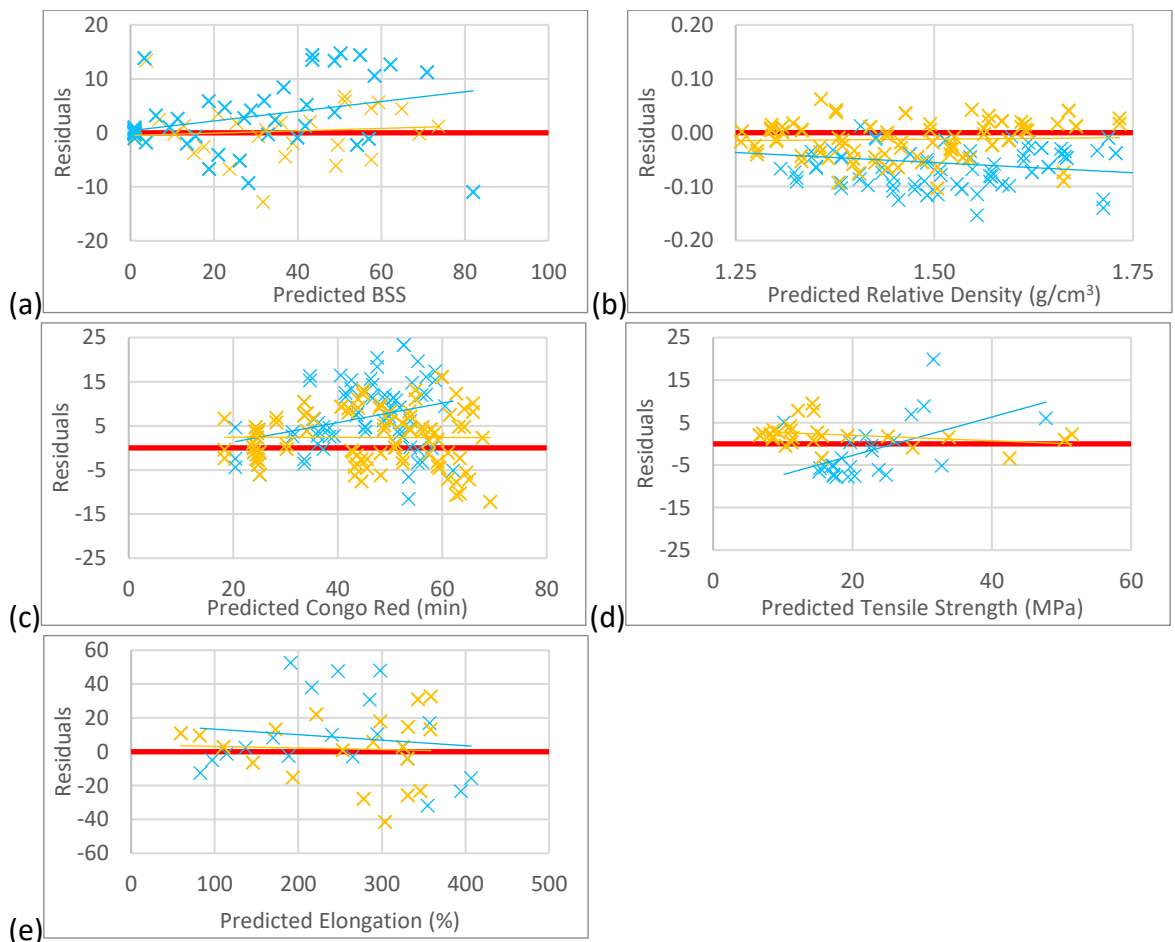


Figure 7-14: Residual plots for each test completed (BSS (a), Relative Density (b), Congo Red Heat Stability (c), Tensile Strength (d), and Elongation at yield (e)) following the correction factors added to the model.

Table 7-15: Table of the initial and corrected root-mean-squared values showing the percentage differences.

Test	Initial RMS	Corrected RMS	Percentage Difference
BSS	6.37	4.38	-31.30
Relative Density	0.07	0.04	-46.58
Congo Red Heat Stability	9.33	6.58	-29.49
Tensile Strength	5.11	1.98	-61.23
Elongation at Yield	25	20	-21.09

7.3.3 Phase 4 Test Data

Following the testing completed on the Phase 1 and Phase 2 data and the correction factors added to the model, a further ten formulations were produced and tested to validate the model in Phase 4.

7.3.3.1 FT-IR Spectroscopy

The spectroscopic data from Phase 4 was collected to provide further testing and validation of the model. Figure 7-15 gives the graphs of the actual raw material levels versus the predicted raw material levels for each of the raw materials used, as well as the residual plot for each raw material. Strong linear correlations were found for each raw material, with the poorest correlation being for the filler, with the R^2 value being 0.8 as opposed to the >0.96 found for the other raw materials. Figure 7-15 (a) and (d) show all negative residuals, showing that the model is overpredicting the raw material concentration for the PVC resin and stabiliser package. Out of the four raw materials, the results found for the plasticiser concentration, seen in Figure 7-15 (b), were the most promising, with the trendline between the actual and predicted concentrations being close in value. The residual plot shows all positive residuals, with most being close to zero. These results suggest that there is a slight under prediction on the plasticiser concentration. Figure 7-15(c), shows the graphs for the filler concentration, the residuals are all positive and show that the model has underestimated the filler concentration present in the PVC compound.

The results found here, whilst promising, demonstrate that further work is required to refine the model to account for the variations that could occur within the industry, such as, production runs, equipment, and companies.

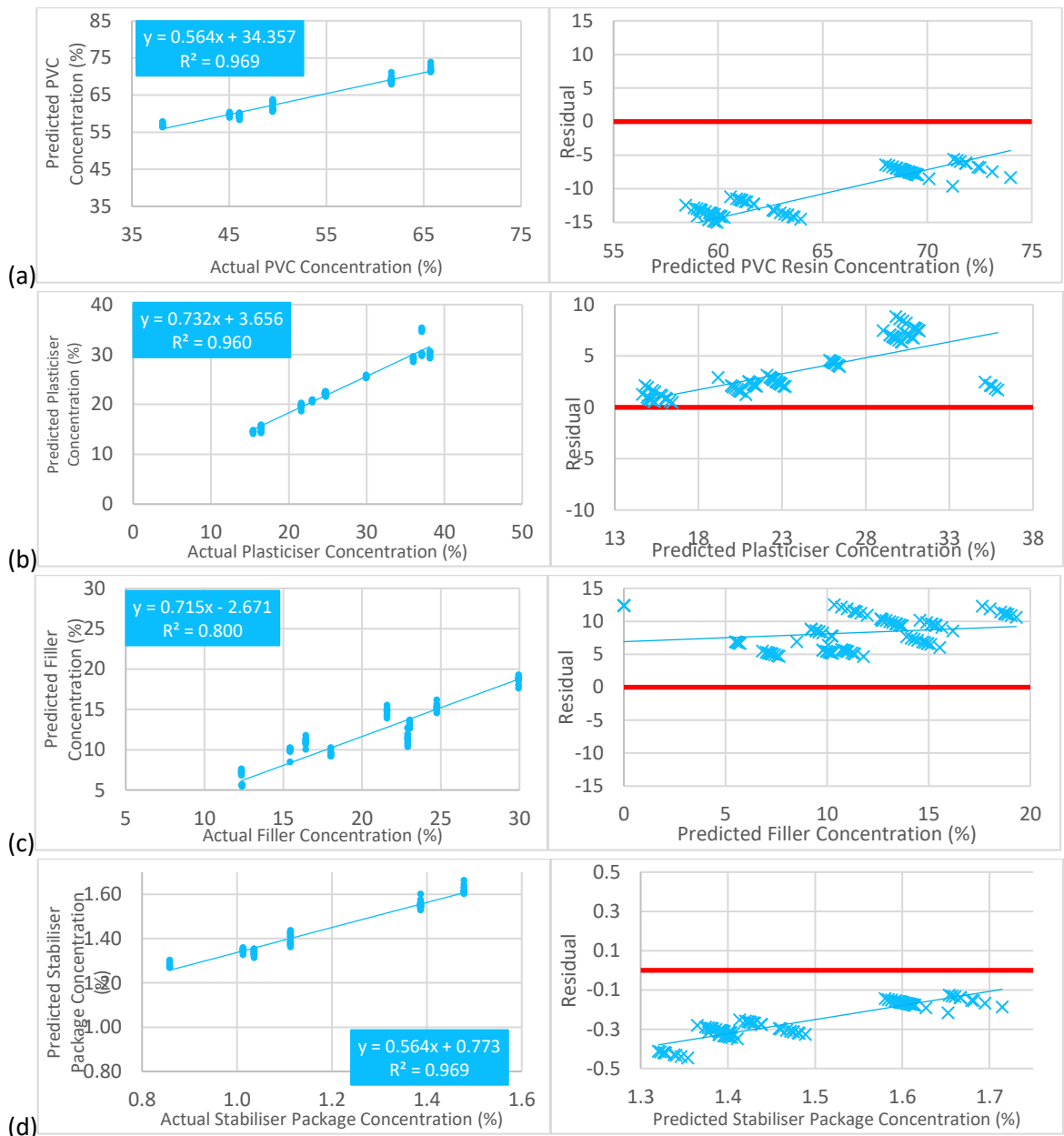


Figure 7-15: Shows the graphs for the actual concentrations versus the predicted concentrations, and the residual plot for the predicted concentration for each raw material (PVC Resin (a), Plasticiser (b), Filler (c), and Stabiliser Package (d)), for the Phase 4 data.

7.3.3.2 Industrial Testing

Figure 7-16 gives the graphs for the industrial properties, with the graphs on the left giving the actual values versus the predicted values and the graph on the right giving the residuals for each predicted test. Figure 7-16 (a), (d) and (e) all gave very strong linear correlations with R^2 values greater than 0.905. Figure 7-16 (b) and (c) also gave clear linear correlations, however the datapoints were more spread, with R^2 values of 0.719 and 0.777 being obtained. The residual plot for Figure 7-16 (a) shows that most of the residuals are on or

around zero with only three points outside of this general trend. The residual plot for Figure 7-16 (b) shows that the values all fall around the zero, the maximum variation is -0.07, 5.15% of the original values. The residual plot for Figure 7-16 (c) shows values around the zero, the residuals are more spread than those seen in (b), however all but two of the datapoints lie within 10%. The residual plot for Figure 7-16 (d) shows the datapoint lie around the zero line, with all but three residuals being within the 10% range. The residual plot for Figure 7-16 (e) shows that most the residuals lie within a 10% range, with the residual values all lying around the zero line.

From these predictions, when the extremities are removed (DOTP at 25 PHR and 100 PHR concentration) the BSS results fall within an 11% range, the relative densities fall within a 4.9% range, the Congo red heat stabilities lie within a 15% range, and the elongation at yield falls within a 15% range (with a single outlier removed). The tensile strength results are all predicted to be lower than the actual results by 10%. The Phase 4 samples were produced using a two-roll mill, therefore it is possible that the predictions for the tensile strength are only accurate for samples that are produced via techniques that provide higher gelation levels, such as two-stage mixing and plant production. In future iterations, this is something that could be considered as an option within POLEMERS.

The result found for the Phase 4 data suggest that predictions can be made that lie within an acceptable range, especially when considering the BSS and relative density, the two most tested material properties on GP pPVC.

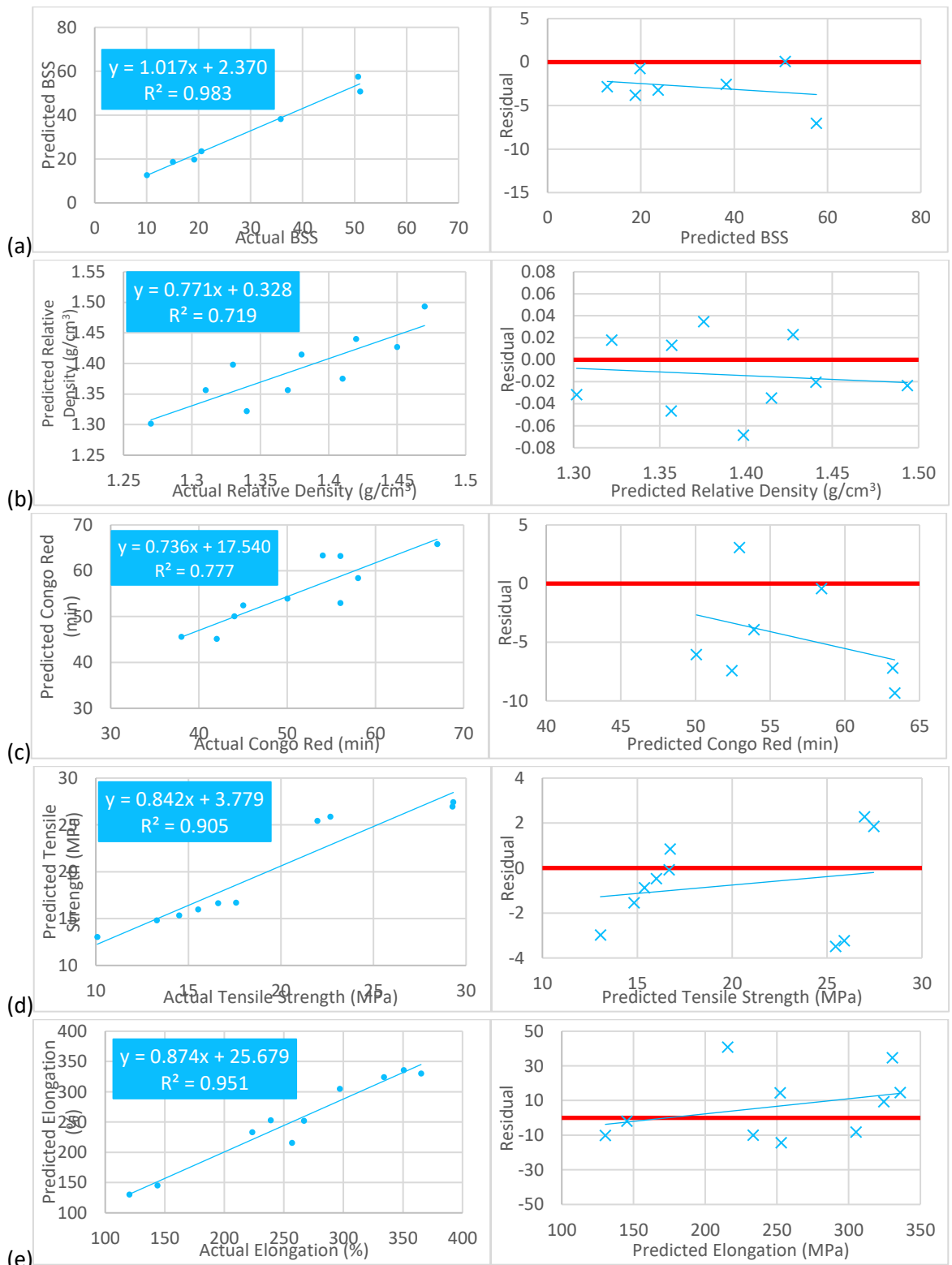


Figure 7-16: Graphs for the actual versus the predicted values, and the residual plot for the predicted values for each test completed (BSS (a), Relative Density (b), Congo Red Heat Stability (c), Tensile Strength (d), and Elongation at yield (e)), for the Phase 4 data.

7.4 Chapter 7 Conclusions

Chapter 7 describes the process and data analyses required to create an industry-relevant model, POLEMERS, that enables (1) the prediction of pPVC formulation and (2) the prediction of the properties of a pPVC formulation. In addition, the model was tested for its robustness and accuracy. It was found that:

1. POLEMERS successfully predicted the BSS and relative densities of both the test and validation data, to within an industrially accepted standard, as well as providing Congo red heat stabilities and elongation at yield values to within 15%.
2. It has been shown that the production method does in fact need to be accounted for when considering the tensile strength of the material, as significantly lower values were obtained when using samples that were milled rather than mixed.
3. When using FT-IR spectroscopy, whilst there are strong correlations present between the predicted and actual values, the predicted values were significantly better on the test data than with the training data. The test data was created and analysed in the same production batch as the training data, therefore further work is required to determine whether this is due to the production method, the testing or simply something that would need to be compared with a standard material during each test.

Overall, a good basis for POLEMERS has been laid out in this chapter, and with further testing using both laboratory and industrial samples POLEMERS could be further refined to allow for successful prediction of both the raw materials from FT-IR and the material properties from the raw materials within 10% tolerances.

A part of the main objective was to create a predictive model that could reduce cost to the company when developing and/or testing new materials. It is therefore considered important to provide some indication on the cost savings that companies could look forward to when using the POLEMERS. Thus chapter 8 describes the cost savings aspect.

8. Financial Implications

The process of testing an incoming competitor PVC compound and developing an alternative can vary, depending on the application or how specialised the application of the material is. For the purposes of this study only general-purpose flexible PVC compound will be considered, with the testing being in line with that completed within this study.

Once the sample is received, test specimens are prepared: for BSS, a 10 mm plaque is needed and for tensile testing a 2 mm plaque is required. Assuming sufficient material is received, this process can take 20 – 30 minutes to prepare each sample. BSS is tested after 7 days as per BS 2782-3: METHOD 365A (BSI, 1976b). Tensile testing is completed after 24 hours as per BS 2782-3:METHODS 320A TO 320F (BSI, 1976a), to test a full set of 5 test specimens typically takes 30 minutes. Congo Red testing will be conducted, this take takes around 5 minutes of preparation, unless repeats are required – the test itself varies depending on the material being tested but does not require a member of staff for most of the time. In total the process of classifying a competitor material usually has a turnaround time of 7 days and utilises 105 minutes of technical staff time for each set of test specimens. Once a base set of results have been obtained for the competitor sample, the first round of prototype formulations can be produced. First each formulation is weighed out into a beaker, the amount of time this takes depends on the complexity of the PVC compound. In this instance we shall consider a general flexible PVC compound, where this task would take an experienced team member 15 minutes per sample (including clean up). Each sample must then be processed on a two-roll mill to produce a uniform PVC hide, and this takes a further 15 minutes per sample (including clean up), if the mill is already at the required temperature. From there the prototypes are tested as per the same procedure as the competitor material. In total the process evaluating a prototype material usually has

a turnaround time of 7 days and utilises 135 minutes of technical staff time, per the relevant repeats and testing for each sample.

In total the time taken to classify a material and prepare and evaluate an alternative is a minimum of 14 days and 240 minutes of technical staff time. This assumes that there is only one material and only one prototype to test. Organising work into campaigns can help to reduce turnaround time by working on many projects at once, however this does not significantly increase the technical staff time within those 14 days.

Cost in terms of staffing is difficult to approximate, however using an average technologist salary of £25 000 at 37.5 hours per week the testing would cost £51.28 ($12.82 * 240/60$).

Whilst this is not a significant cost to a company when viewed in isolation, this example is a bare minimum and when there are 100s of these being processed by a R&D lab each year, the costs could quickly add up. Time is also a crucial factor here, as usually if a customer is looking to find a new supplier, they would send samples out to multiple potential suppliers. Being the first to respond to the request, leads to a much higher chance of acquiring the business, in many cases customers are seeking a resolution to an issue they are facing.

Using POLEMERS, the initial testing portion of the process can be cut down to just testing the sample using the ATR-FT-IR (5 minutes) and then inputting the spectral data into the model. This should take no more than 20 minutes in total (technical staff time and turnaround time). Once a formulation has been predicted, the technical staff will then be able to produce a sample and test the prototype for suitability. This in theory would reduce the technical staff time down to 125 minutes and 7 days turn around. Over a period, with the model being validated and updated, this could be reduced further.

Using an average technologist salary of £25 000 at 37.5 hours per week the testing would cost £26.67 ($12.82 * 125/60$). This represents a 47.99% reduction in staff costs and frees up 115 minutes of technical staff time per samples to work on more technical projects.

9. Conclusions and Further Work

The work within this thesis has successfully created the first two iterations of the predictive model: POLEMERS, which can allow for the streamlining of the pPVC formulation process using spectroscopic techniques.

9.1 Aims and Objectives

We hypothesised that accurately deconvoluted vibrational spectroscopic data can form the basis of a predictive model that can be used to predict either formulation composition or properties of pPVC. Therefore, the aim was to create a comprehensive databank for different pPVC formulations to feed into the model and thereby determining relationships between raw material quantities, properties, and spectroscopic intensities. This has been achieved through the six objectives outlined in section 0.

Objective 1: Determine the properties to be evaluated alongside suitable spectroscopic techniques, based on industrial standards. The parameters were determined through research and knowledge of PVC compound and are those tested within industry on flexible PVC compound. These parameters are BSS, relative density, Congo red heat stability, and tensile properties. FT-IR and Raman spectroscopy identified as suitable for analysing these properties, with FT-IR being deemed the most suitable spectroscopic technique.

Objective 2: Identify the raw materials having the biggest impact on the materials properties identified in Objective 1. K70 PVC resin was selected as the most used PVC resin in GP pPVC. DOTP plasticiser was used due to it being the most commonly occurring non-phthalate, a phthalate was not chosen due to restrictions in certain applications. GCC was chosen as the most used filler. A generic calcium-zinc stabiliser package was also selected. Other raw materials were considered in Phase 3. Overall, the plasticiser concentration had the biggest impact on the properties, followed by the filler concentration.

Objective 3: Create 96 different PVC formulations based on the raw materials identified in and complete testing on these to create a databank for interrogation. An extensive databank was created, with multiple repeats being completed for each property, with consideration being made to look at additional factors, such as other raw materials and the less commonly used higher and lower concentrations of raw materials.

Objective 4: Create a predictive model using the data, using statistical relevance to inform formulations from the spectroscopic results, and the properties from the formulation. POLEMERS was successfully created and gave promising results in the testing and validation steps. However, further work, alongside industry partners is required to ensure that the model is truly fit for purpose.

Objective 5: Test the model on for accuracy, repeatability, and applicability in industry, using a test dataset. Phase 4 provided testing against additional laboratory samples. POLEMERS will also be offered for trial use to the PVC industry in exchange for feedback as to determine its practicality within PVC formulating and QC applications.

9.2 Contributions

Overall, this work has:

1. Successfully created for the first time a predictive model, POLEMERS, that has the capability of predicting multiple raw material levels and multiple material properties of pPVC, for GP applications. With the basic properties being predicted to industrially acceptable levels on the second iteration of POLEMERS.
2. Created a databank of multiple pPVC formulations and material properties, alongside spectroscopic data, which has not only been used for the creation of POLEMERS but can be used to identify further relationships in the data and inform the industry.

3. Shown that FT-IR performs better than Raman spectroscopy when looking for a simple prediction of the raw material concentrations in PVC, as well as proving to be the faster and cheaper technique, for which skilled labour is not essential.
4. That POLEMERS has the potential to provide an almost 50% reduction in laboratory staffing costs, as well as freeing up significant time per sample that would be better utilised for tackling the bigger issues facing the PVC industry.

Furthermore, POLEMERS and the associated work, has filled a gap in knowledge.

Within the literature there is limited research into the use of spectroscopic techniques to predict the raw material concentrations in PVC compound, especially when considering multiple raw materials. This project has extensively considered the spectral analysis of pPVC, as well as discovering the issues associated with this, such as batch to batch variation.

In addition to this the extensive literature survey completed, in section 0, demonstrated that whilst testing is done on pPVC, this is generally done in isolation looking at one property, one raw material, or one application, not as a whole considering the influence of multiple raw materials, on multiple properties for multiple applications. This is something that has been achieved within this thesis.

Within the industry it provides a way for anyone to formulate PVC, removing the current gatekeeping steps that are often found within the PVC industry, as well as providing cost savings at a time when prices are volatile, and any saving is crucial to a company.

9.3 Limitations

Like with all predictive models, POLEMERS does have its limitations, and with it being only in its second iteration, further work is required.

1. POLEMERS currently works most effectively in the midranges. At higher and lower raw material concentrations it can struggle due to less investigation into these extremities.
2. POLEMERS is currently only set up for DOTP when using spectroscopy. When using just

the property prediction it works for multiple plasticisers – though this is limited and should be completed with caution.

3. POLEMERS currently is limited in its functionality with specialised raw materials. However, basic data can be collected.
4. Currently further work is required to fully refine the model, especially when considering the spectroscopic predictions.

Each of these points are areas where further work can be completed to create a more robust and multifunctional model to better serve the PVC industry.

9.4 Practical Implications

This research has provided a simple to use, easily accessible model that allows anyone to formulate PVC with specific properties with relative ease. The only required training would be in using the FT-IR and the model itself. This therefore removes the requirement of multiple formulation chemists, allowing the job to be done by anyone with this basic training. This can significantly lower the cost of staffing. It significantly speeds up the process of analysing samples and creating matches, allowing customer satisfaction both in terms of speed and being fit for purpose.

9.5 Further Work

Based on the findings and limitations identified in this study, several avenues for further research could be pursued to enhance the effectiveness and applicability of POLEMERS. Firstly, expanding the dataset used for model development could lead to more robust predictions across a wider range of formulations and properties. This could involve incorporating data from industrial samples, thereby validating the model's performance in real-world scenarios. Additionally, including a broader spectrum of raw materials and concentrations in the dataset would enable POLEMERS to accommodate a greater diversity of PVC formulations commonly encountered in industry practice.

Moreover, refining the spectroscopic techniques employed in data collection could enhance the accuracy and reliability of POLEMERS predictions. Investigating advanced signal processing algorithms or alternative spectroscopic methods could offer improvements in resolving spectral features and reducing noise, thus enhancing the model's predictive capabilities. Furthermore, exploring the integration of machine learning algorithms into the model architecture could enable POLEMERS to adapt and self-improve over time, capturing complex nonlinear relationships between raw materials, properties, and spectroscopic data.

Lastly, conducting extensive validation studies across multiple PVC applications and processing conditions would provide valuable insights into the generalizability and robustness of POLEMERS. Collaborating with industry partners to deploy the model in real-world settings and gathering feedback from practitioners would facilitate iterative refinement and optimization. Additionally, investigating the scalability of POLEMERS to handle large-scale production scenarios and its compatibility with existing quality control systems would be essential for its seamless integration into industrial workflows. Overall, these future research directions aim to elevate POLEMERS from a promising concept to a practical and indispensable tool for the PVC industry.

9.6 Overall Conclusions

The main contribution of this research is the creation of a novel predictive model, POLEMERS, that takes spectroscopic data, creates a PVC formulation, and predicts its properties within 10 minutes. However, it has also provided:

- A contribution to the wider understanding of PVC and its testing with spectroscopic techniques.
- A contribution to the wider understanding of PVC and properties and the relationship between these as well as each other.

10. References

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11. Appendix

The full appendices can be found in the [POLEMERS](#) folder.