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FACULTY OF SCIENCE

WMG

Engineering Doctorate

Innovation Report

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ABSTRACT

There are numerous techniques that can be used for the decoration of polymeric substrates, dye sublimation, self-colouring, paint spraying, granular injection paint technology, pad printing, in-mould decoration and hot foil stamping. Dye sublimation was selected for this research as it was found to be both the most relevant technology area for IDT Systems Limited and the least understood. It is a customisable digital process which uses specialist Cyan, Magenta, Yellow and Black (CMYK) inkjet-able dyes that are transferred into a substrate via a carrier. During the process heat is applied which transforms the dyes from a solid into a gas phase. Analysis of literature identified a number of knowledge gaps, which are addressed during this research and detailed in this report.

Initial experimentation concluded that the sublimation dyes can penetrate a range of commercially available amorphous polymers, comparably to semi-crystalline types. These findings dispute previously published work, but these also lacked rigorously recorded methodologies to confirm comparable data. All of the materials, equipment and methodologies used throughout this research were therefore developed in this report.

Further detailed experimentation was completed, using amorphous polycarbonate, (PC) and semi-crystalline polybutylene terephthalate, (PBT) focusing on the process time and temperature to understand their influence on the level of dye penetration. The results revealed that increasing the process temperature and time improves the level of dye penetration and that comparable penetration levels were noted at 140-180 ^{o}C. Further research identified the importance of free volume in the polymer, this increases in size and connectivity as temperature increases above the glass transition points. Additional experimentation confirms that the free volume enables the dyes to penetrate into the polymer.

Characterisation of the CMYK sublimation dyes was completed using Differential Scanning Calorimetry enabling the thermal transitions to be identified. Visual experimentation confirmed that the dyes start and finish sublimation between 145-210 ^{o}C.

As no software tool existed to visualise the dye penetration, one was developed using MatLab. The tool imports and then interpolates the data and graphically outputs it for the user. This allows a quicker set up time of the process and reduces the number of samples to be destroyed.

As a direct result of the innovations described in this report, the industrial sponsor has benefited with an increase in commercial exploitation. Aspects of this research have been published, presented and a patent has been published, details are provided within.

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Academic Mentors-Professor Gordon Smith, Dr Vannessa Goodship
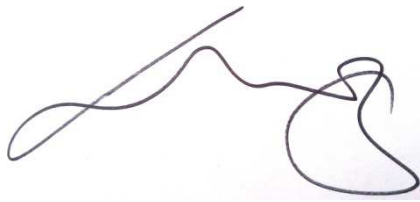
Industrial Mentor-Mr Peter Woodd

INDUSTRIAL SPONSOR FOR THIS RESEARCH

IDT Systems Limited / The Factory / Dippenhall / Farnham / Surrey / GU10 5DW, Tel 01252 726080 / Website www.idt-systems.com

DECLARATION

I hereby declare that all of the work contained in this report was produced by the author and that none of the work has been previously submitted for an academic degree. All sources of quoted work have been referenced accordingly

Mr Kylash Makenji

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FREQUENTLY USED ABBREVIATIONS

The list below contains some of the commonly used abbreviations found within this report. .

B	Blurry
C	Cyan
DEG	Di-ethylene Glycol
DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimetry
F	Faint
IMD	In mould decoration
K	Key (Black)
M	Magenta
^{o}C	Degrees Celsius
OK	Okay
PALS	Positron annihilation lifetime spectroscopy
PBT	Polybutylene terephthalate
PC	Polycarbonate
PET	Polyethylene terephthalate
PP	Polypropylene
T_C	extrapolated completion temperature
TC	Transfer carrier
TD	Thermal damage
T_{E1}	1st extrapolated onset temperature
T_{E2}	2nd extrapolated onset temperature
T_g	Glass transition temperature
T_m	Melt transition temperature
T_{P1}	1st temperature peak
T_{P2}	2nd temperature peak
T_{P3}	3rd temperature peak
Y	Yellow

1. INTRODUCTION

At the dawn of this programme it was evident that very little quality research was available regarding the dye sublimation process analysis of literature reviews yielded large knowledge gaps. The sponsor company, who has been a part of this technology for over 15 years, confirmed that this was the state of affairs within this industry.

The aim of the Engineering Doctorate, (EngD) is to create and exploit new innovations in the dye sublimation process. This is achieved by understanding the process fundamentals enabling industry to select from a wider range of materials and ensure the dyes are optimally processed.

The dye sublimation process relies on a considerable amount of testing and evaluation time to generate a consumer ready component (Barrow, 2010). The software based dye penetration visualisation tool discussed in section 7 was developed by the author to reduce the costly sampling and measuring time, currently taken.

Controlling the dye penetration depth is one important aspect of the process; a deep level of penetration would make the substrate very hard wearing, whilst a shallow level would make the substrate easily worn so that it can be frequently replaced. Finally this research is designed to develop a suitable methodology for the characterisation of new substrate materials, dyes and process. The objective of gaining all of this knowledge is to both satisfy the academic rigor required by the EngD degree and benefit the industrial sponsor through new commercial exploitation opportunities.

1.1. INNOVATIONS FROM THIS RESEARCH

The list below contains the innovations the author has created from the research during the period of the EngD. The innovations are:-

- The capability to use amorphous polymers in the dye sublimation process, where they were previously thought to be unsuitable, thereby extending the range of material usage for IDT Systems Limited, (IDT) to exploit with this technology

- The ability to use the time and temperature parameters to control the level of dye penetration into the polymer, thereby allowing IDT to control the lifetime of the surface decoration

- The establishment of a methodology for assessing the suitability of new polymers in the dye sublimation process, thereby allowing IDT to quickly assess new materials.

- Identification of the key thermal transitions of the dyes in the process when sublimation starts and ends and linking this knowledge to the dye sublimation process. This allows IDT to establish quality control of their raw material suppliers.

- The creation of a visualisation tool in Matlab to establish ideal processing set up conditions for the acceptable level of dye penetration. This reduces wastage of parts during evaluation.

- Further as a contribution to knowledge this work has also highlighted the importance of free volume as a mechanism for the transportation of the dye into and through the polymer.

1.2. RESEARCH DISSEMINATION

This work has been disseminated in varying guises with the kind permission of the industrial sponsor. The first opportunity was at the Foresight Vehicle Conference (Makenji, 2009) where the preliminary research findings were disseminated. Secondly the findings of the literature review and the results of the initial experimentation were published in a peer reviewed journal (Makenji, 2011) this covered elements of **portfolio submissions 1-3**.

Another method of dissemination was the University of Warwick 2010 poster competition where the author won a runner up prize. The poster contained the salient points of the research objectives and findings; these had to be verbally conveyed to a judging panel (Makenji, 2010).The final mode of dissemination was the publication of the patent titled "Improvements in Dye Sublimation" detailed in **portfolio submission 6** (Makenji and Baumber, 2010). The patent describes a new method for processing the dye sublimation technology. It was conceived as a result of the experimentation completed in **portfolio submission 3**.

1.3. RESEARCH EXPLOITATION AND IMPACT

This research has enabled IDT to commercially exploit the use of polymers previously thought of as being unsuitable for the process. One of the recent exploitations is the offshoot business, "Who's On Your Case" where consumers can order personally decorated polycarbonate mobile phone cases (It's my case, 2011, Who's on your case, 2011). Table 1 shows IDT Systems customer projects, where the research has been of direct or indirect commercial benefit. These are considered in this context as they have enabled IDT Systems to test, trial or use semi-crystalline polymers in the process where this was previously thought as being unsuitable. Alternatively this research has enabled them to applying the innovations from the EngD which enables by them to achieve aesthetically pleasing components in a short space of time without significant destructive testing.

In relation to this research and the impact of the innovations to IDT Peter Woodd, CEO, wrote *"Kylash's association with IDT-Systems Limited during the period of his Engineering Doctorate has created a broad range of benefits that has allowed our company to be more competitive in the global space. The results from his work have enabled us to be more innovative in the market place and secured us a prominent position for some years to come. We are number one in this market, we have a reputation for quality. It would be easy to see that the contribution to the bottom line is in excess of 15%. He was very professional in all his dealings with our supply chain and customers alike. He gained a great deal of respect for his attention to detail and delivering a fast and effective solution in a timely manner"* (Woodd, 2011)*.*

Table 1 IDT Customer list and website details

Customer	Website details
IDT Systems, Who's on your case	www.whosonyourcase.com
Uncommon	www.getuncommon.com
Microsoft	www.microsoft.com
Dell	www.dell.com
ATI	www.atigunstocks.com
Casemate	www.case-mate.com
Flextronics	www.flextronics.com
Tom Tom	www.tomtom.com
Oakley	www.oakley.com

1.4. RESEARCH METHODOLOGY AND REPORT STRUCTURE

This innovation report is structured to follow the progress of the Engineering Doctorate and the **portfolio submissions**. Firstly there was a need to research the various techniques for the surface decoration of polymers, including materials, process and industrial practises. This was completed using secondary data sources such as peer reviewed journals, publications, articles, books and the internet. Most of this was completed using the University of Warwick library resources and data bases such as Science Direct and Compendex. IDT was an invaluable source of knowledge, given the lack of published data and vast amount of industrial experience they have with the surface decoration of substrates. This combined use of academic and industrial resources led to the identification of knowledge gaps, located in section 2.1 of this report. Due to the lack of published knowledge with the dye sublimation process these gaps were addressed by designing and completing primary experimentation.

Section 3 details all of the experimental work undertaken including the methodologies, materials and equipment used. Section 4 describes the experimental results the analysis and discussion is located in section 5 and 6. An illustration of the methodology is shown in Figure 1.
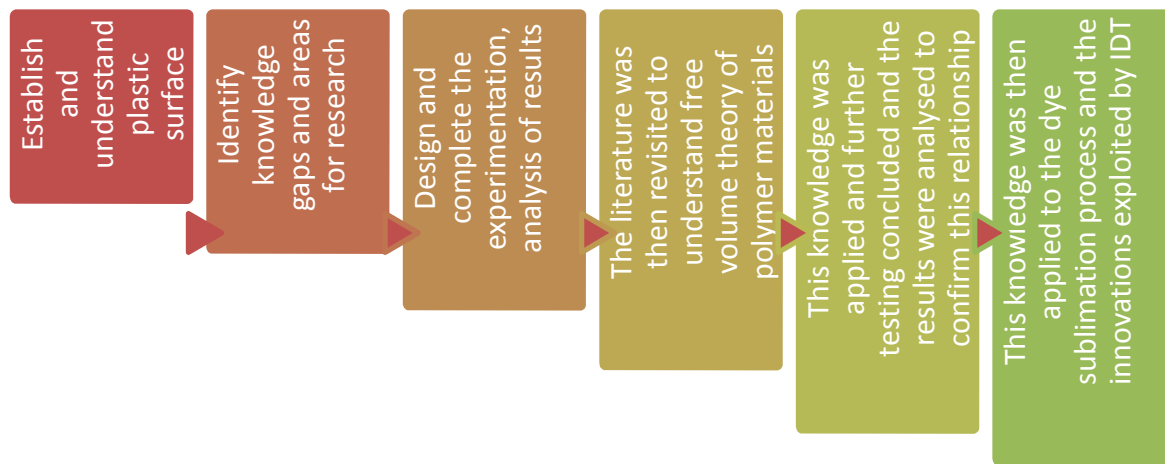
Figure 1 The Engineering Doctorate research methodology

Section 7 presents details on a dye penetration depth visualisation tool developed using MATLAB. Section 8 contains overall conclusions of the research and experimentation. Section 9 highlights the benefits of the research to IDT and includes a section which identifies some financial gains of using the optimised process highlighted in this report. Section 10 contains suggested further work and the references are located in section 11. Table 2 lists the **portfolio submissions** completed during the EngD, these will be referred to for further explanation or detail within this report.

Table 2 Details of the portfolio submissions

N°	Portfolio submission title	Report section
1	Colourful Decoration Techniques for Plastic Injection Moulded Parts Suitable for Mass Customisation	2 & 2.1
2	Initial Dye Sublimation Experimentation, Methods and Materials	3, 4 & 5
3	The Penetration Performance of Sublimation Dyes into Semi-crystalline and Amorphous Polymers	3, 4 & 5
4	The Thermal Characteristics of Sublimation Dyes	3, 4 & 6
5	Visualisation of the Dye Penetration Depth using Matlab	7
6	Patent	1.3
7	Journal publication	1.3
8	Personal Profile	n/a

2. OUTCOMES FROM THE LITERATURE REVIEW

Injection moulding of polymers is a common manufacturing technique used to create parts (Xanthos, 2002). These components sometimes require surface decoration to make them more appealing to consumers. A literature review of current practises was completed, to select a decoration technique which could be used to mass customise parts manufactured from polymers. Ideally the process should not have too many process stages, be environmentally friendly and low cost, whilst achieving an aesthetically pleasing surface. Dye sublimation, (Adams, 2007, Sherman, 2005) self-colouring of polymers (Margolis and Meyer, 1986) wet paint spraying, (Stoye and Freitag, 2007) granular injection paint technology, (Smith and Easterlow, 1996) pad printing, (Berins. M, 1991) in-mould decoration, (Love and Goodship, 2002) and hot foil stamping (Margolis and Meyer, 1986) technologies were explored. Details of the processes, material used, advantages and disadvantages are provided in **portfolio submission 1**. Direct inkjet printing is also possible but it has limitations when compared to dye sublimation. It has a low print resolution, the dyes sit on the surface of the polymer and do not penetrate into it and finally the decoration can only be completed on substrates with a flat geometry (Barrow 2010).

Dye sublimation was selected as the ideal surface decoration technology for plastic parts based on a number of criteria. The process needs no pre or post treatments, it is environmentally friendly and equipment costs are not prohibitive. It can achieve aesthetically pleasing surface decorations and allows the user to mass customise (Adams, 2007, Sherman, 2005). Dye sublimation achieves these criteria better than the other technologies explored.

Dye sublimation is a digital process. Inkjet printing technology is used and the print head lays down one droplet of dye at a time onto a transfer carrier (TC) until an image is generated. The dye colours are delivered individually as cyan ("C") magenta ("M") yellow ("Y") and black ("K") (collectively known as CMYK). The system can achieve up to 16.7 million colours (Anon, 1997). The dyes are transferred into the polymer substrate by means of sublimation, where the dye materials start in a solid phase and transform into a gas state when heat is applied (Ortolani, 2006, Storey, 1975).

The digital nature of the process is highly suitable for mass customisation enabling individual part decoration without incurring unnecessary set up or additional costs (Adams, 2007, Barrow, 2010). The state of the art systems can enable the process to be used on complex geometry components, by vacuum forming a TC around the substrate prior to the dyes being sublimated.
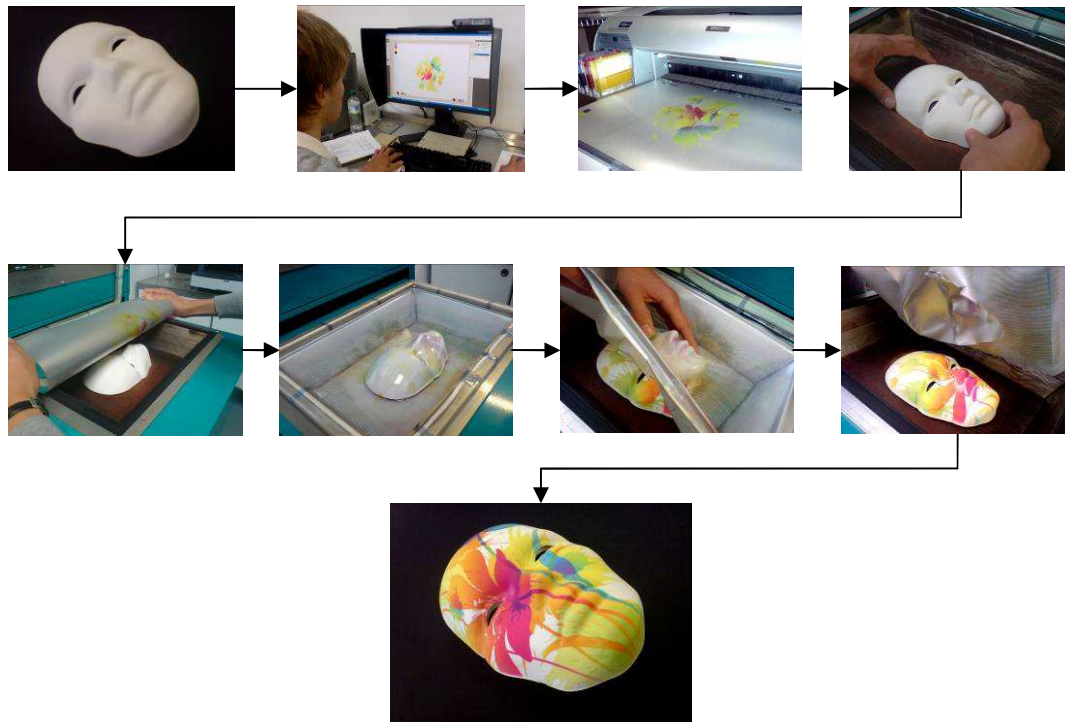
Figure 2 The IDT i-SDS transfer process

For the purpose of describing the technique the author will outline the i-SDS process developed by IDT, illustrated in Figure 2. The first image shows the blank plastic substrate, the second shows the digital image which is then printed onto the TC using the special sublimation dyes. The plastic substrate is loaded into the transfer press with the TC placed directly above it. Heat is used to soften the TC enabling it to be thermoformed to the substrate by applying a vacuum pressure. Further heat is used in the process enabling the dyes to sublimate whereby they change from their solid condition into a gas. The gas is then able to penetrate the plastic substrate. The transfer press is cooled, the TC is removed and discarded and the printed image is visible on the surface of the substrate. There is little published literature regarding the process, it appears that most of it is anecdotal (Barrow, 2010).

2.1. DYE SUBLIMATION KNOWLEDGE GAPS

Dye sublimation has very little published research available to review; it does appear to be a very "cottage" type of technology and would benefit with contribution to practise. Analysis of the literature highlights a number of knowledge gaps, which have been listed below. The objectives of this research are to address the knowledge gaps through experimentation and through analysis and insight provide innovations that IDT can exploit.

(1) Data presented by Adams (Adams, 2007) illustrated in Figure 3, show that the dyes sublimate into semi-crystalline polymers more than the amorphous polymers. No reason is given for this condition. The author will investigate by means of experimentation.
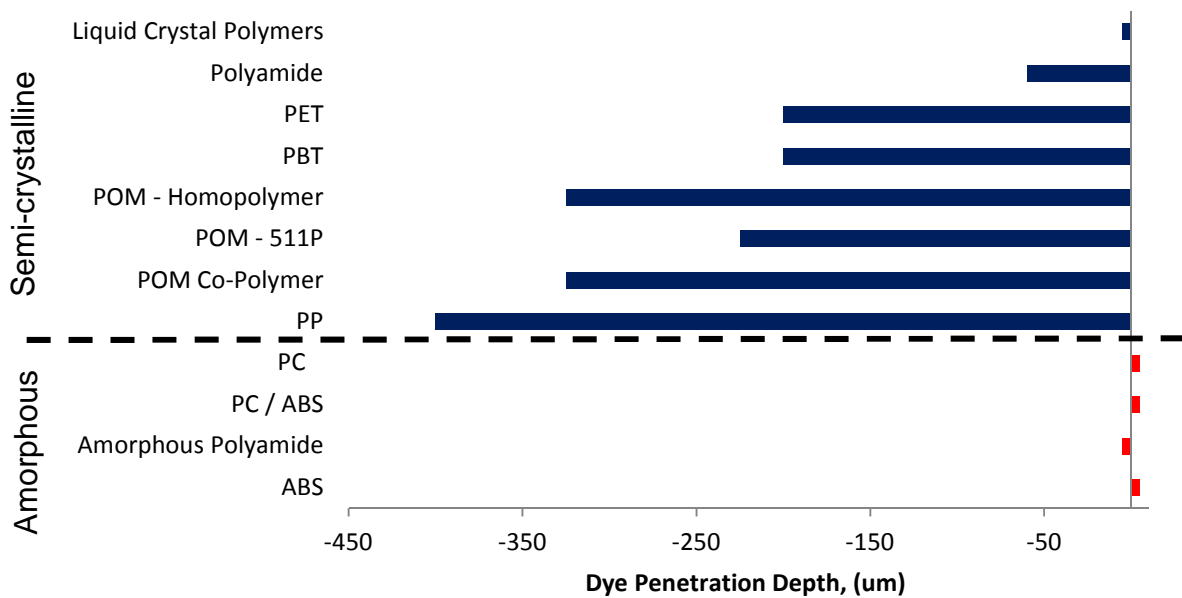
Figure 3 Dye penetration depths published by Adams (Adams, 2007)

(2) The data presented by Adams (Adams, 2007) does not describe how the CMYK colours perform in different polymers. This is another area of investigation undertaken.

(3) No published information is available about the thermal characteristics of the sublimation dyes and how these relate to the substrate polymers. Experimentation to characterise the sublimation dyes will provide this knowledge.

(4) There are no commercially available tools for the visualisation of dye penetration depth. Such a tool could be used to speed up product development time and reduce the number of parts physically destroyed.

3. INTRODUCTION TO EXPERIMENTATION UNDERTAKEN IN THIS RESEARCH

The data generated and published by Adams (Adams, 2007) does not indicate either how the substrates were processed or how the dye penetration depths were measured, the author contacted both Larry Adams (Adams, 2010) the publication author and Christophe Chervin (Chervin, 2010) of DuPont Engineering polymers, the original source of data, but neither responded to the requests. This could have been for a number of personal reasons or that the data was industrially sensitive. It was decided by the author to design a series of experiments which would yield new data to further academic knowledge and industrial innovation. The materials, methods and testing are described within this section.

3.1. MATERIALS USED IN THE EXPERIMENTATION

This section describes the materials used in this research.

3.1.1. THE SUBSTRATE POLYMERS

The polymeric materials used to create the experimental substrates are listed in Table 3. These materials were selected in order to gain knowledge of dye penetration behaviour in a range of commercially available amorphous and semi-crystalline materials.

Table 3 Experimental polymer substrates

Type	Polymer	Abbreviation	Manufacturer	Grade
Amorphous	Polycarbonate	**PC**	Sabic	ELX 1414
	Acrylonitrile butadiene styrene	**ABS**	ABSCOM	F350
	Polystyrene	**PS**	Total Petrochemicals	PS 1540
	Acrylic	**PMMA**	LG Chem	IF 850
Semi-crystalline	Polypropylene	**PP**	Bassel	HP551M
	High density polyethylene	**HDPE**	BP	HD802GA
	Polyamide	**PA**	Vydyne	21SPC
	Polybutylene terephthalate	**PBT**	DuPont	S600F20

The materials selected have a commercial interest to IDT as these could extend the range of materials available for customer projects (Barrow, 2010). The polymer materials were prepared by injection moulding into substrate plaques approximately 160 mm square and 3 mm thick. This was completed on a Battenfeld 110 T injection moulding machine; 10 parts were produced of each material type to ensure any variations occurring from the manufacturing process where kept to a minimum.

3.1.2. THE SUBLIMATION DYES

The commercially available dye materials used in these experiments were supplied by Sawgrass and were of the SubliJet IQ type, consisting of a standard CMYK colour profile. The composition for all colours was established from the material safety data sheet (Sawgrass, 2008). Sawgrass were kindly asked to supply further information regarding the dye materials; however they refused to do so, on propriety grounds (Cobb, 2010). The "dye material" is recognised to be all of the components shown in Table 4. The water component is used as a carrier in the inkjet system it quickly evaporates when printing has been completed (Meyer, 1975, Lee, 2005).

There are other commercially available sublimation dyes however as this work is to fully understand the process for IDT, only their preferred supplier was selected for this project. It is thought that different suppliers of dyes would produce similar results, this could be confirmed with further experimentation, as noted in section 10.

Table 4 Dye material composition

Number	Component	Quantity
1	Dye	<5%
2	Organics	<20%
3	Di-ethylene Glycol (DEG)	<25%
4	Glycerine	<25%
5	Water	Remainder

3.1.3. THE TRANSFER CARRIER

The TC supplied by IDT is an amorphous polyethylene terephthalate film 190 μm, thick +/-10%. It has two coatings applied onto one side the first is a metallic barrier and the second is a release coating. The metallic layer acts as a barrier to prevent the dye from penetrating the film. The release coating enables the dyes to be applied to the film prior to it being used in the transfer process. The TC was printed onto using an Epson 4400 printer at a resolution of 600 dots per inch, with the CMYK dyes, using a standard print image as shown in Figure 4, once printed the films were dried.

CYAN-C

MAGENTA-M

YELLOW-Y

BLACK-K

Figure 4 The CMYK test print

3.2. EXPERIMENTAL DESIGN AND EQUIPMENT USED

This section describes the experimentation methods undertaken in this research. First initial experiments were conducted to understand how much dye penetration was possible into a range of polymers. The result from the initial experimentation prompted the need for extended dye penetration depth experimentation using amorphous and semi-crystalline polymer substrates. Finally there was a need to characterise the sublimation dyes so that it could be used in-conjunction with the findings from the penetration experimentation.

3.2.1. THE DESIGN OF THE INITIAL DYE PENETRATION EXPERIMENTATION

Initially experiments were undertaken to understand how much the dyes penetrate amorphous and semi-crystalline polymers. The D6.3 transfer press, supplied by IDT was used to decorate the substrate materials listed in Table 3.
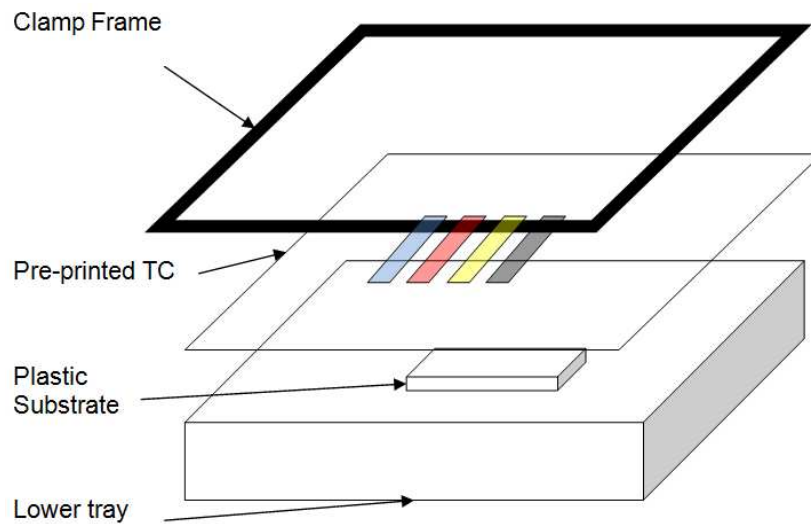
Figure 5 Schematic of the transfer press arrangement

The process was set up by firstly placing the substrate into the lower tray of the transfer press, the printed TC is placed directly above and held using a clamp frame. A schematic of the arrangement is shown in Figure 5.

For the purpose of these experiments the parameters, detailed in Table 5, were set to typical values considered for the decoration of polymer substrates. Tests detailed in **portfolio submission 3** established that the "substrate surface temperature" is identical to the "Temperature" shown as parameter 4.

Table 5 Dye sublimation experimentation parameters

N°	Parameter	Setting	Description
1	Thermo Softening Point (°C)	70	Heat the TC to the "Thermo Softening Point" to enabling vacuum forming
2	Film Soften Time (seconds)	5	"Film Soften Time" enables an isothermal condition of the TC
3	Vacuum Dwell (seconds)	15	The "Vacuum Dwell" is the vacuum forming time.
4	Temperature (°C)	175	Heat is applied until the "Temperature" is reached where the dyes sublimate.
5	Time (seconds)	45	Heat is applied for the "Time" allowing dye penetration into the substrate.
6	Cooling Temperature (°C)	65	The system is cooled to the "Cooling Temperature" enabling safe handling
7	Vacuum Pressure (bar)	-0.6	"Vacuum Pressure" is applied, allowing the TC to form over the substrate

An image of a decorated substrate is shown in Figure 6 and an illustration of the D6.3 transfer press is shown in Figure 7.

Figure 6 Photograph of the dye sublimation decorated component

Figure 7 IDT D6.3 transfer press

3.2.2. DESIGN OF THE EXTENDED DYE PENETRATION EXPERIMENTATION

Literature analysis shows that the key parameters of the dye sublimation process are temperature and time. It is understood that these directly affect the level of dye penetration into the substrate. The literature identifies that the process temperature can range from 137.7-300 ^{o}C (Adams, 2007, Slark and Hadgett, 1999) and the time from 0.12–10 minutes (Shearmur et al., 1996, Chandler, 2007) presenting a wide range of operation, for further details see **portfolio submission 3**. What is unknown about these parameters is how they affect the level of dye penetration into the polymer substrate.

To better understand the effect of temperature and time on the level of dye penetration further experiments were designed and undertaken. This was completed using semi-crystalline PBT and amorphous PC substrates Table 3. For these experiments the **Temperature** was set at 140, 160, 180 and 200 ^{o}C. At each setting the **Time** was set at 20, 40, 60 and 80 seconds, Table 5 parameters 4 and 5. All other settings and the equipment arrangement was as described in section 3.2.1.

3.2.3. THERMAL CHARACTERISATION OF THE SUBLIMATION DYES

The dye materials sublimate during the "Heat" phase of the dye sublimation process. Analysis of the literature revealed no information regarding the thermal characteristics of the dye materials and how they affect the level of dye penetration into the polymer. Therefore to characterise the dyes in a thermal condition, experimentation was completed using a Differential Scanning Calorimetry (DSC).

Before testing, the water in the dye material specimen (Table 4, component 5) was evaporated to mimic the process naturally occurring following inkjet printing. To establish the water content of the dye materials, weight loss experiments were completed. The dye materials were individually filled into 100 µl crucibles and heated in a small oven, from 25–100 ^{o}C, using a 2 ^{o}C/min ramp rate. The specimens were then maintained at 100 ^{o}C for a further 120 minutes to ensure that all of the water had evaporated and the weight loss was recorded. The experiment was completed three times for each of the dye colours, the results are presented in Table 8, the water content is calculated to be 55-73%.

It is considered that during these experiments other volatiles in the dye composition may have evaporated however for this experimental work it is assumed that the weight loss is solely the result of water.

Figure 8 Image of a Mettler Toledo DSC1

The DSC experiments were completed using a Mettler Toledo DSC 1 with an auto sampler, located in the Physics Department, University of Warwick; as illustrated in Figure 8. All of the experiments were completed using a temperature range of 25–300 $^{\circ}$C, this range was selected to establish the effect of thermal loads on the dye material at low and elevated temperatures. A 36 $^{\circ}$C/min ramp rate was used for the primary experiments thereby emulating the D6.3 transfer press. These were repeated 3 times for the CMYK dye materials.

To establish the effect of heating ramp rates on the dye materials, additional experimentation was completed using the "Y" dye material. Only this dye was used at it was believed that all the CMYK dyes would behave similarly. The ramp rates used were 5, 10, 20, 30, 40, 50, 60, 70, 80 and 100 $^{\circ}$C/min. Only one experiment was completed at each ramp rate.

All of the DSC experimentation was completed in a N_2 environment to eliminate the effect of oxidisation of the dye materials at high temperatures, (Hatakeyama and Quinn, 1999).

Visual confirmation of the thermal transitions of the dye was also completed. Initially a number of setup experiments were undertaken to establish a test methodology. Approximately 1 mg of the dye material was thinly laid onto aluminium foil, covering approximately 2 cm^2. The specimens were individually heated in a small oven at a 36 ^{o}C/min ramp rate, until the transition temperatures were reached as detailed in Table 8.

The specimen was allowed to become iso-thermal for 1 minute at the transition temperature before being inspected and photographed by the author. The enthalpy values were established using the Mettler Toledo Star software. Further details can be found in **portfolio submission 4**.

3.3. THE OPTIMUM LEVEL OF DYE PENETRATION

A high level of dye penetration in a component is desirable so it can endure a harsh and abrasive environment ensuring it will survive its intended lifetime. Alternatively a low level of dye penetration can bring a level of obsolescence to the component, ensuring that the decoration wears and the article is replaced regularly thereby generating additional revenue for the manufacturer. This may be desirable with certain product types such as push on mobile phone covers, which are considered to be a sacrificial part of the mobile phone (White, 2010).

The ideal dye penetration depth is unknown at present as no literature exists where an acceptable level is proposed. Alternative plastic surface decoration technologies such as spray painting (Stoye and Freitag, 2007) and in-mould decoration (IMD) (Love and Goodship, 2002) provide a "protective layer" over the substrate. For spray painting this is 25-40 μm and for IMD it is 25-75 μm. This "protective layer" is considered to be the depth of material that could be initially worn away before the substrate material is revealed.

As a benchmark of acceptable dye penetration depth into the polymer substrate it is proposed by the author:-

- <25 μm=unsuitable
- 25–75 μm=optimum
- >75 μm=considered to be an unnecessary improvement

Following this research the author proposes a revised acceptable level of dye penetration of 15-75 μm, see section 9.1.

3.4. DYE PENETRATION MEASUREMENT METHODOLOGY

From each decorated substrate the CMYK colours were cut into individual samples approximately 5 mm x 5 mm and the surface was microtomed ready for optical microscopy.

Dye penetration was viewed using a Zeiss, Axio Scope A1, optical microscope at 5x magnification; dye penetration was established using Axio Vision software. Where possible a minimum of five dye penetration readings were taken for each of the decorated substrates. It is noted that on some of the decorated substrates there was insufficient dye penetration, making measurement extremely difficult. For these specimens a low number of readings were recorded.

Lack of variability in the dye penetration across the decorated substrate was established in **portfolio submission 2**, therefore only one sample was required for optical microscopy for each of the decorated substrates. All of the specimens were prepared, measured and stored at a constant temperature of 21 ^{o}C. An illustration of the "Y" dye penetration into PBT, processed at 180 ^{o}C, 60 seconds is shown in Figure 9.
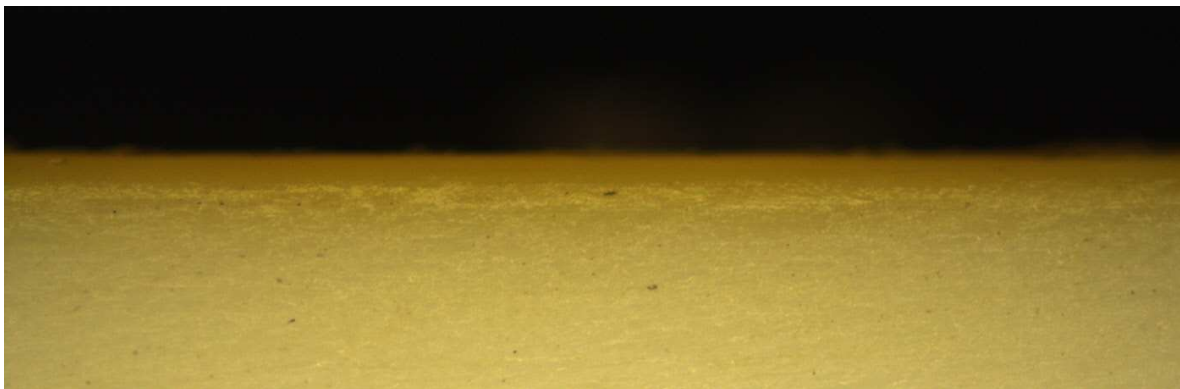
Figure 9 Illustration of "Y" dye penetration into PBT

4. EXPERIMENTAL RESULTS

This section details the experimental results from the experimentation described in section 3.

4.1. THE INITIAL DYE PENETRATION EXPERIMENTAL RESULTS

The average dye penetration values from the initial experiments described in section 3.2.1 are displayed Table 6, detailed results are available in **portfolio submission 2**.

Table 6 Average dye penetration depth measurements by material and colour

Type	Polymer	Dye penetration depth (µm)				Average
		C	M	Y	K	
Amorphous	PC	54	62	62	62	60
	ABS	5	6	31	19	16
	PS	62	62	77	38	60
	PMMA	154	46	46	138	96
Semi-crystalline	PP	18	92	538	77	181
	HDPE	278	194	333	278	271
	PA	115	115	92	62	96
	PBT	62	85	100	62	77

4.2. THE EXTENDED DYE PENETRATION EXPERIMENTAL RESULTS

The averaged dye penetration depths from the experimentation described in section 3.2.2 are shown in Table 7, detailed results are available in **portfolio submission 3**.

Table 7 PC and PBT dye penetration results

Polymer	Temperature (^{o}C)	Dye penetration depth (µm)			
		Time (seconds)			
		20	**40**	**60**	**80**
PC	**140**	0	7.54	16	10.29
	160	14.6	17.51	20	19.51
	180	43.31	48.24	58.02	61.52
	200	65.72	88.06	107.09	115.97
PBT	**140**	2.21	4.78	5.52	6.99
	160	10.83	14.57	18.92	26.64
	180	28.26	37.07	60.31	86.86
	200	131.96	150.05	157.43	179.37

4.3. THE THERMAL CHARACTERISATION EXPERIMENTAL RESULTS

The DSC graphs from the experiments described in section 3.2.3 for the CMYK dye materials are shown in Figure 10. The results show the endothermic kinetic reaction of the dye materials, whereby the dye materials absorb thermal energy (Brown, 2001).
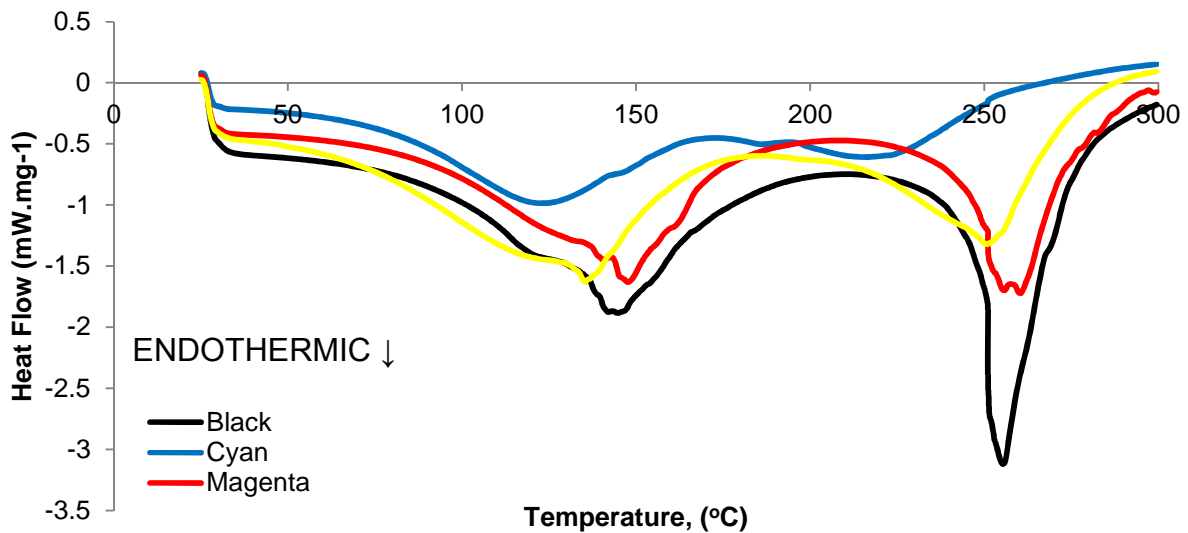
Figure 10 DSC results for all colours

Enthalpy is a measure of the total energy for a thermodynamic system (Hatakeyama and Quinn, 1999). The enthalpy values from the DSC experiments and the thermal transitions (Höhne et al., 2003) are shown in Table 8. Figure 11 illustrates the "K" DSC result, labelled with the thermal transitions.

Whereby:-

- T_{E1}-1st extrapolated onset.
- T_{P1}-1st peak.
- T_{C}-extrapolated completion.
- T_{P2}-2nd peak.
- T_{E2}-2nd extrapolated onset.
- T_{P3}-3rd peak.
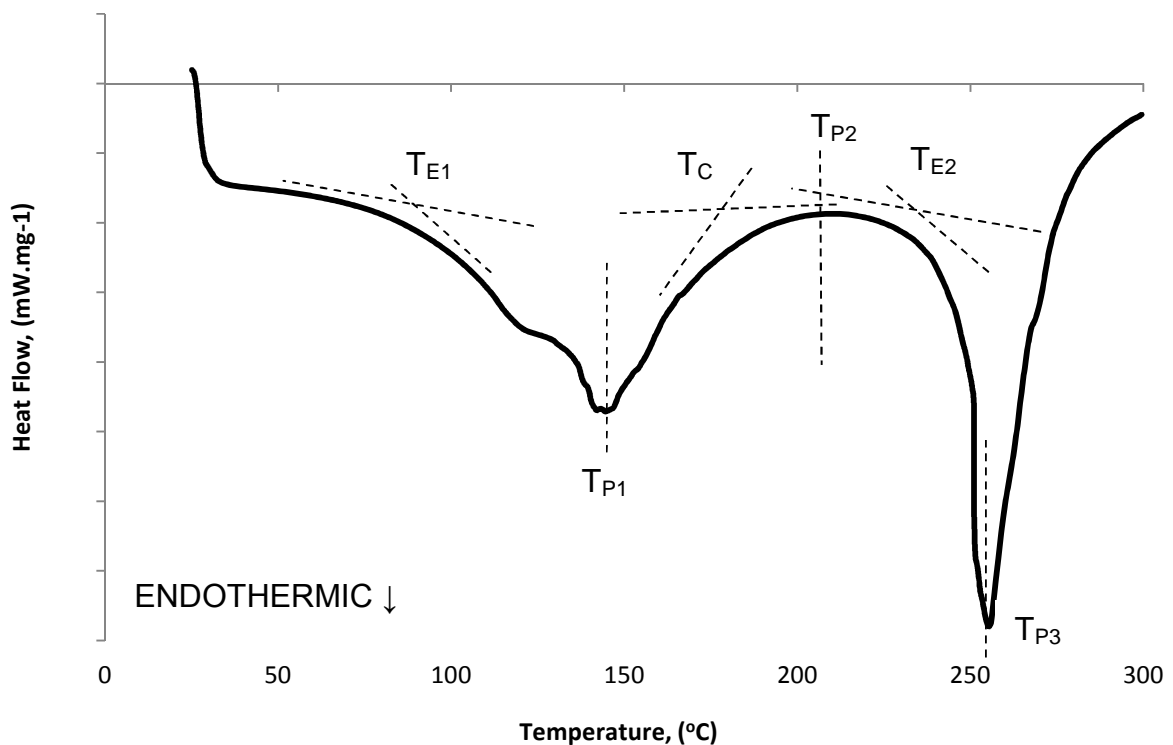
Figure 11 "K" dye material with the thermal transitions labelled

Table 8 Thermal transitions, enthalpy and water content for the dye materials

Thermal transitions	Temperature (°C)				Ideal
	C	M	Y	K	
T_{E1}	80.8	90.2	67.5	90.8	
T_{P1}	119	145	133	142	145
T_C	164	175.2	169.6	181.8	
T_{P2}	172.7	208	185.8	210.3	210.3
T_{E2}	178	224	209	224	
T_{P3}	215	258	247	254	
Enthalpy (J/g)					
T_{E1}–T_{P2}	-209.47	-216.85	-351.10	-212.20	
Water content (%)					
	72.64	63.14	72.13	55.44	

Figure 12 shows the DSC plot for the "Y" dye material with images of the tested specimens at the respective thermal transitions detailed in Table 8.

The results from the experimentation of the dyes detailed in section 3.2.3 show that at 25°C and at T_{E1} the colour remains visibly unchanged. At T_{P1} a slight level of colour fading is evident. At T_C the dye colour has faded indicating that sublimation has occurred. At T_{P2} only a trace of the dye colour is evident. Examination of the dyes heated to T_{E2} and T_{P3} showed no further visual change to the colour. From the results it appears that the dye materials start sublimation at T_{P1} and cease at T_{P2}.
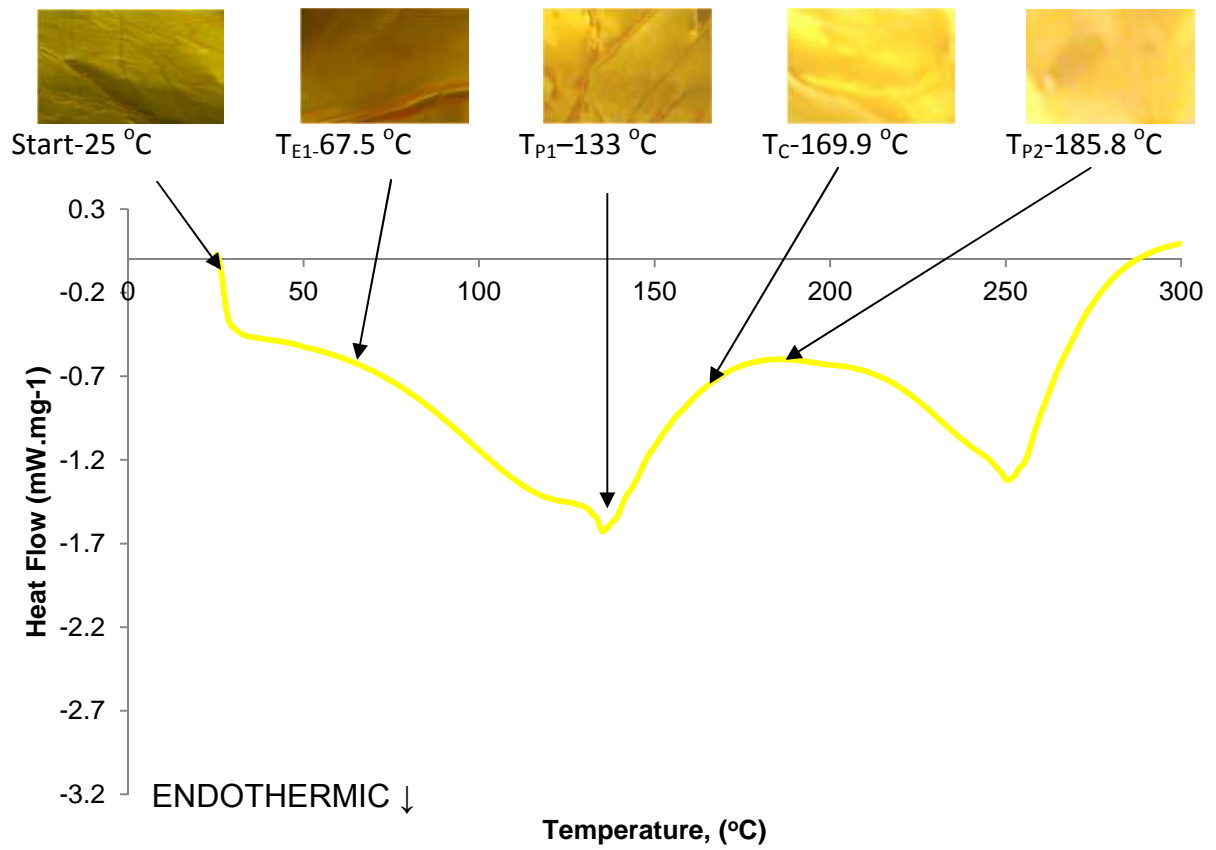
Figure 12 "Y" DSC plot showing the visual effects of the thermal loading

5. ANALYSIS AND DISCUSSION OF THE DYE PENETRATION EXPERIMENTATION

This section analyses and discusses the results of the experimentation outlined in sections 3.2.1 and 3.2.2. The level of CMYK dye penetration into the substrates is appraised as is the surface decoration and condition of the polymer surface. The free volume of polymers is discussed and further experimentation is undertaken to prove the relationship with dye penetration.

5.1. ANALYSIS AND DISCUSSION OF THE INITIAL EXPERIMENTATION

Table 9 contains the data from the dye penetration measurements for different polymer types presented by Adams (Adams, 2007) and the average values for each polymer type established by the author. These values are calculated by averaging the dye penetration measurements for each of the individual colours.

Table 9 Comparison of Adams and the author's initial experimental data

| Polymer | Dye penetration depth (µm) | | |
	Adams data (Adams, 2007)	Average authors data	Difference
ABS	+5	-16	21
PA	-70	-96	26
PBT	-200	-77	123
PC	+5	-60	65
PP	-400	-181	219

In Table 9 the positive (+) value implies that the dye is adding to the specimen thickness, the negative (-) value is where the dye is penetrating into the polymer. From the authors experimental measurements, no increases to the thickness to the specimens were observed.

The two sets of data show disparate values when compared to each other. Considering amorphous PC as an example; Adams illustrates that the process adds 5 µm to the thickness of the substrate, the results from the initial experiments show a penetration of 60 µm equating to a difference of 65 µm. The semi-crystalline PP shows a 219 µm difference between the published and measured values; other disparities are also observed. At no point during this work was any sign of the surface addition as reported by Adams, (Adams, 2007) witnessed.

The differences between the data could be due to the lack of process parameter information and the measurement technique used, making direct comparisons impossible. As previously stated the author was unable to obtain this data from Adams and Chervin (Adams, 2010, Chervin, 2010).

Adams (Adams, 2007) shows negligible dye penetration into the surface of amorphous polymers, implying that the decorated surface would wear quickly. DuPont state that the *"dye does not penetrate and can be scratched off easily, when using amorphous polymers such as PC and ABS"* (Anon, 2005). The significance of this research is that when designers or manufacturers investigate this process, they may rule out this technique, if they base their decision on inappropriate data.

Whilst useful data has been generated from these initial experiments, it highlights the need for further rigorous experimentation to better understand the effect of time and temperature with respect to dye penetration into polymer substrates.

5.1.1. SECTION CONCLUSIONS

Little academic literature is available regarding the dye sublimation process however Adams (Adams, 2007) describes the process and the level of dye penetration into different polymer types. The data from the literature shows that the dyes penetrate semi-crystalline polymers to a significantly greater level than with amorphous polymers types.

Experimentation was conducted by decorating general purpose polymer materials followed by optical microscopy. This established dye penetration measurements which differ greatly from those reported. Due to the lack of rigorous data no methodology was available until established by the author for specimen decoration and the measurement of dye penetration.

The previously published data indicated that the dyes barely penetrate amorphous polymers and in some cases an additive condition occurred. The experimental results from this study show that the dyes penetrate PC up to 65 μm more than previously reported. PP and HDPE show a considerable level of dye penetration, whilst the results suggest that amorphous substrates are comparable to semi-crystalline PBT and PA.

The work published by Adams does not contain any processing information which could have affected the level of dye penetration into the substrate polymers. The author attempted to gain this information but communication with the originator of the data and the author of the publication were unsuccessful.

This work concluded that amorphous polymers are suitable to be used in the process and an acceptable level of dye penetration can be achieved. Whilst meaningful data has been generated from the initial experimentation, it also highlights the need for further work to better understand the effect that process time and temperature have on the level of dye penetration, further details of this work can be found in **portfolio submission 2**.

5.2. ANALYSIS AND DISCUSSION OF THE EXTENDED EXPERIMENTATION

This section analyses and discusses the results from the extended experimentation described in section 4.2.

5.2.1. AMORPHOUS PC

Figure 13, shows the average dye penetration depths of the CMYK colours for the time of 20-80 seconds and the temperatures of 140-200 ^{o}C, the measurement error bars are discussed in section 5.2.6.

The graph shows that an increase in time results in increased levels of dye penetration. The processing time of 0–20 seconds achieves a high level of dye penetration. At the settings of 140–180 ^{o}C, 20–80 seconds the dye penetration has increased by 30–50%, however at 200 ^{o}C, 20–80 seconds the level of dye penetration almost doubles.

The results show that raising the temperature increases the dye penetration depth, which has increased by 112%, 194% and 78% when the process temperature has increased from 140–160, 160-180 and 180-200 ^{o}C respectively. One important point is that the graph does not show the "additive" nature of the dye on the surface of the polymer as shown in Figure 3 (Adams, 2007).
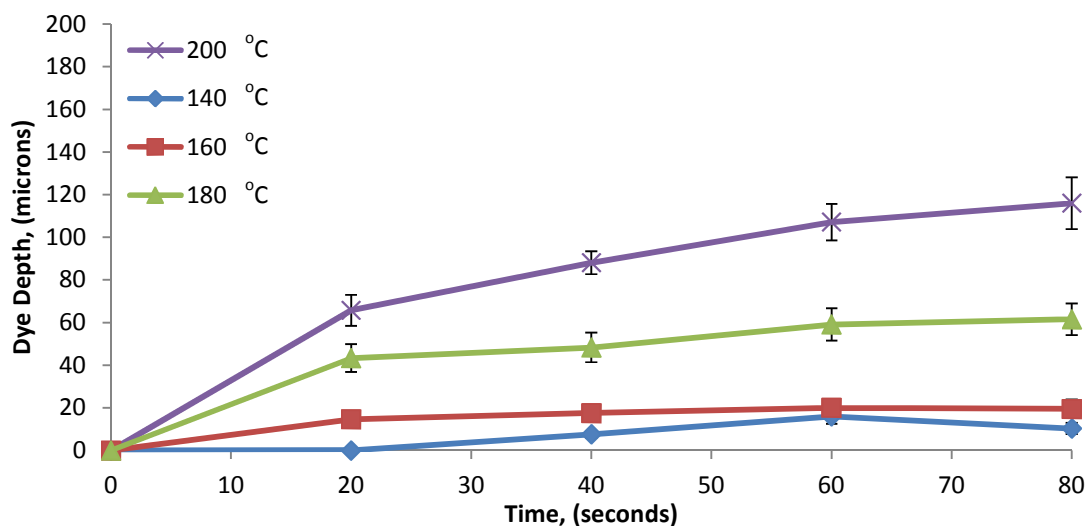
Figure 13 PC Average dye penetration depths with error bars

Table 10 shows a visual chart of the CMYK colours which gave the deepest or shallowest dye penetration at the given experimental settings.

Table 10 PC Visual chart of deepest and shallowest dye penetration depths

Sublimation temperature (°C)	Deep				Shallow			
	Time (seconds)							
	20	40	60	80	20	40	60	80
140	-	Y	M	K	-	M	K	C
160	C	C	C	K	Y	Y	K	M
180	C	M	M	M	K	K	K	K
200	C	K	M	M	K	M	K	K

The results show that at 140 °C, 20 seconds there is no dye penetration, at 40–80 seconds the "Y", "M" and "K" colours show a high level of penetration at the different processing times. At 160 °C, the "C" dye gives the best level of penetration at 20-60 seconds, at 80 seconds the "C" is only 1.48 µm less than the "K" dye. At 180 °C the "M" dye displays high levels of penetration when processed for 40-80 seconds. The results also show that at 200 °C, for 60-80 seconds "M" provides the deepest level of penetration. Overall during the first 20 seconds the "C" dye gives the deepest level of penetration at 160-200 °C.
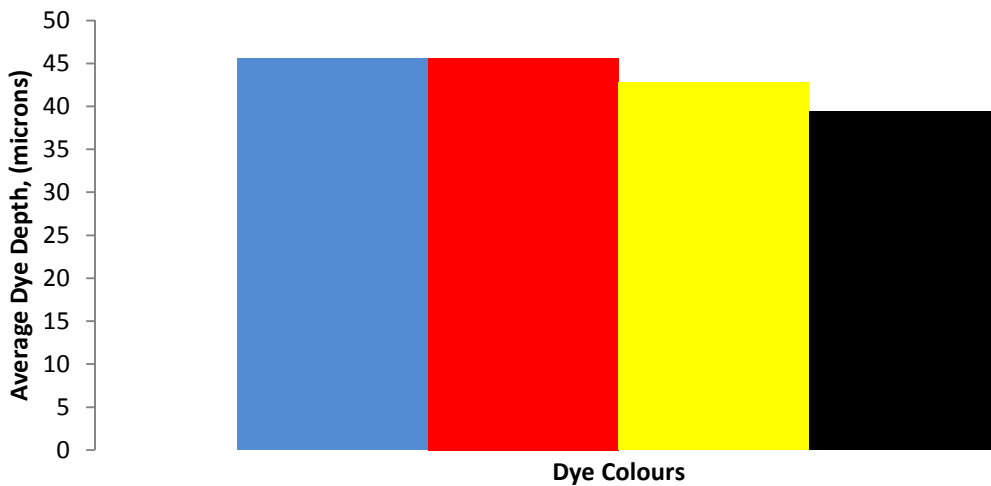
Figure 14 PC Average dye penetration measurements for CMYK colours

Figure 14 shows the average dye penetration depth measurements in the PC for each of the CMYK colours, the data is taken from all of the process temperatures and times. The range between the highest and lowest average is 6 µm representing a variation of 13%, which could be deemed as significant if a constant dye penetration depth is required through all of the CMYK colours, "C" gives the highest average value and "K" gives the lowest.

There is no clear pattern as to which dye gives the shallowest results. However, At 160 $^{\circ}$C the "Y" dye provides the shallowest penetration at 20-40 seconds. At 180 $^{\circ}$C the "K" dye gives the lowest level of dye penetration across the range of different processing times.

5.2.2. SEMI-CRYSTALLINE PBT

The average dye penetration results are shown in Figure 15, the error bars are discussed in section 5.2.6. The graph illustrates that time increases lead to an improved dye penetration depth, the largest occurs in the first 20 seconds giving an average of 43 µm across the CMYK colours. Increasing the process duration to 40-60 seconds gives a further 9 µm increase per 20 seconds. Increasing the time from 60-80 seconds provides a further 15 µm of penetration.
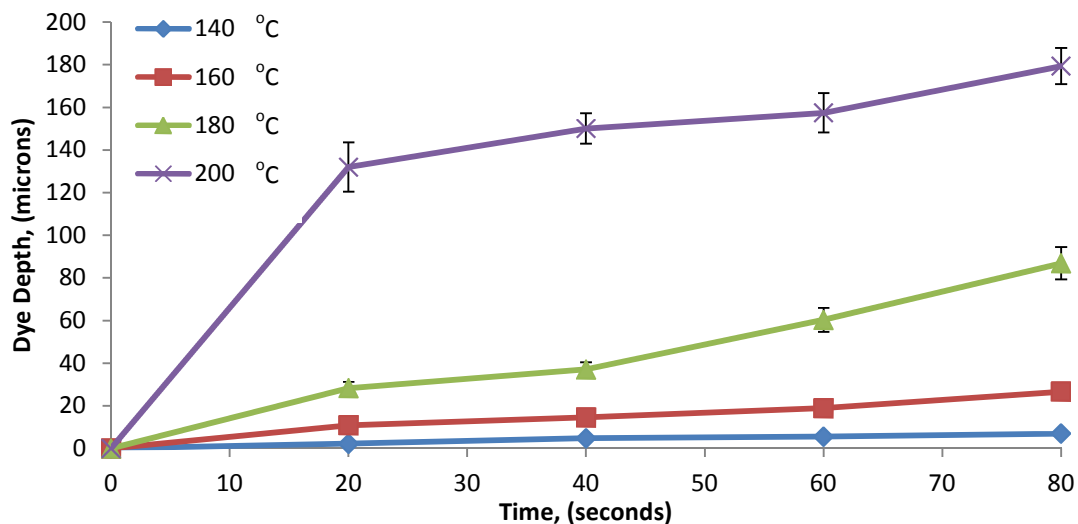
Figure 15 PBT Average dye penetration depths with error bars

The results show that at 140 ^{o}C the level of dye penetration is unacceptably low at 6.99 μm. At 160 ^{o}C using 80 seconds of time and at all of the experiments conducted at 180–200 ^{o}C, dye penetration is recorded to be greater than 25 μm. The best level of dye penetration occurs at 200 ^{o}C, providing an average depth of 123 μm, three times greater than at 180 ^{o}C and nine times more than at 160 ^{o}C.

Table 11 shows a visual chart of the CMYK colours which gave the deepest or shallowest dye penetration at the given experimental settings. At 140 ^{o}C, 0-40 seconds the "K" dye gives the deepest values, with "M" giving significantly increased value at 60 seconds. At 160 ^{o}C the "K" dye gives the deepest measurements at 60-80 seconds. At 200 ^{o}C the "M" dye gives the best readings at the higher processing times.

Table 11 PBT Visual chart of deepest and shallowest dye penetration depths

Sublimation temperature (^{o}C)	Deep				Shallow			
	Time (seconds)							
	20	40	60	80	20	40	60	80
140	black	black	red	black	-	red	blue	yellow
160	yellow	blue	black	black	blue	black	blue	blue
180	yellow	red	black	blue	black	yellow	blue	red
200	yellow	blue	red	red	black	black	blue	black

During the first 20 seconds the "Y" colour gives the deepest level of dye penetration indicating that it goes into the polymer before the other colours. Additionally it is noted that at the temperatures 140–160 ^{o}C, 60 and 80 seconds the "K" dye gives the best level of penetration into the polymer, illustrating that at the lower temperatures this colour penetrates better when compared to the other dyes.

At 140 ^{o}C the readings were taken with difficulty as very little dye had penetrated the polymer. At 160 ^{o}C the "C" colour penetrates the least at 20, 60 and 80 seconds signifying that at this temperature dye penetration ceases earlier than the other colours. At 180 ^{o}C there is no real pattern of which colour penetrates the least. At 200 ^{o}C the "K" dye provides the least penetration illustrating that this colour ceases penetration the earliest. The results show three patterns emerging:-

- 1st-"C" penetrating shallowest when processed at 160 ^{o}C
- 2nd-"K" penetrates the shallowest when processed at 200 ^{o}C
- 3rd-"C" gives the shallowest depth, 60 seconds at all temperatures.

The graph in Figure 16 shows the average dye penetration measurements for each colour across the range of temperatures and times using the PBT polymer. It shows that there is only 4 µm difference between the "M" and "K" dyes, which are the maximum and minimum level of dye penetration retrospectively. This is not envisaged to be a significant value as it only equates to 5-16% of the "target" dye penetration depth.

Figure 16 PBT Average CMYK dye penetration measurements

5.2.3. COMPARISON BETWEEN THE PC AND PBT RESULTS

Figure 17 displays a graph of the average dye penetration depth measurements for the PC and PBT by temperature. The graph shows a similarity in the results between the PC and PBT when processed at 140-180 $^{\circ}$C. At 200 $^{\circ}$C there is a large difference in measured dye penetration depth where the PBT has 60 µm more than the PC.
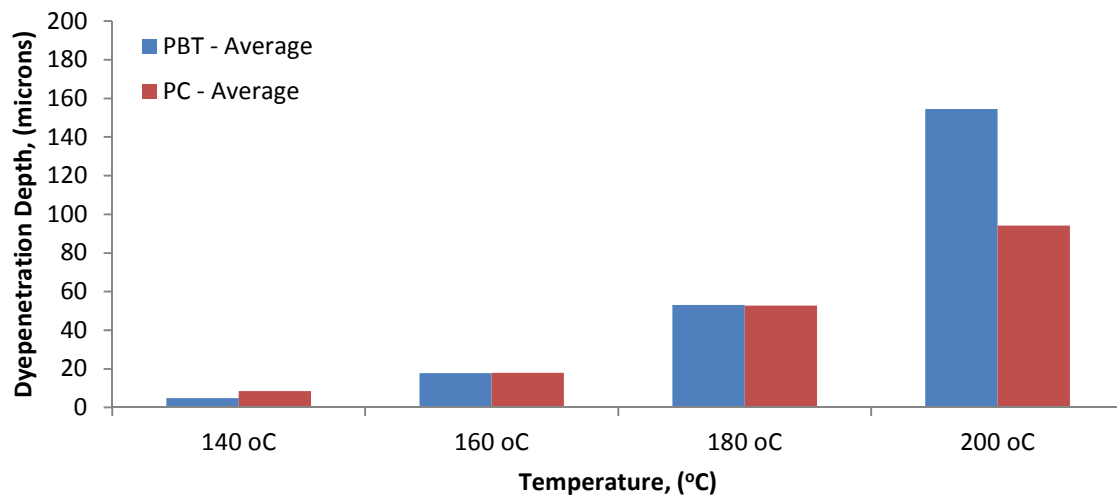
Figure 17 PC and PBT Average dye penetration depth measurements

5.2.4. RATE OF DYE PENETRATION

Figure 18 illustrates the calculated average rate of dye penetration for the PC and PBT polymers. The graph shows that both polymers have a similar rate of penetration when processed at 140–180 $^{\circ}$C. At 200 $^{\circ}$C the rate of penetration for the PBT is 58% greater than the PC. For both materials the highest rate of penetration occurs when the process is operated at 200 $^{\circ}$C during the first 20 seconds, further details can be found in **portfolio submission 3**.
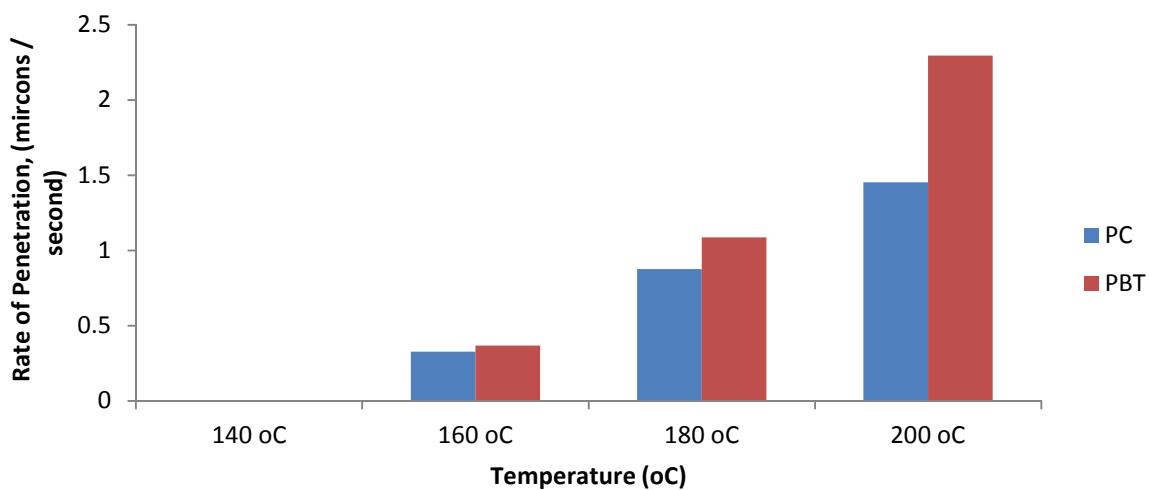
Figure 18 PC and PBT average rate of penetration

5.2.5. FREE VOLUME WITHIN POLYMERS

Free volume theory states that there are varying holes present between the polymer molecules. The free volume quantity is the difference between the actual volume and the excluded volume at a specified temperature and pressure (Simha and Carri, 1994). If the proportion of free volume is increased it becomes interconnected in such a way that the polymer takes on the characteristics of a micro-porous material.

Such polymer types are considered and used for molecular separation and sieving applications (Budd et al., 2005a, Budd et al., 2005b, Budd and McKeown, 2010). E.g. hydrogen, nitrogen and oxygen are successfully separated from the atmosphere by the use of polymeric membrane technology (Veith, 1991).

The transport properties of small molecules in and through polymers are important because of the effect a molecular penetrant can have on the properties of a polymer. Barrier polymers are used when the aim of the material is to inhibit transport of the penetrating molecule. Controlled release polymers are used when transport of an active molecular agent is required to migrate out of the polymer in a prearranged method. Membrane polymers are used where a preferential transport of one molecular component is required. The permeability of a small molecule through an amorphous polymer membrane while in a glassy state is usually low (Budd et al., 2005a).

When the polymer is in a rubbery state the permeability is much higher. Polymers in the rubbery state have an increased free volume which enables high diffusion coefficients, but their ability to be selective as to which molecules can penetrate through the polymer is low. Rubbery polymers are most commonly used for their ability to separate large organic vapour molecules from smaller gas molecules, because of their high solubility selectivity (Budd et al., 2005a). Research suggests that diffusion in a rubbery polymer is the result of redistribution of free volumes within a matrix and migration of the penetrant among these free volumes. Diffusion can therefore only occur if a hole exists that is large enough for a penetrate molecule to enter (Rezac and John, 1998) restated by Lutzow and Willmore (Lutzow et al., 1999, Willmore et al., 2006).

The free volume is constant while the polymer is in the glassy state and is calculated to be 2.5% (Budd et al., 2005a). However there is change in the expansion coefficient at glass transition temperature (T_g) which corresponds to the increase of the free volume.

Figure 19 is illustrated in many texts (Budd et al., 2005a) re-iterated by Ward and Seitz (Ward and Sweeney, 2004, Seitz, 1993). The graph illustrates that the occupied volume increases with temperature rises, throughout the glassy and rubbery states.
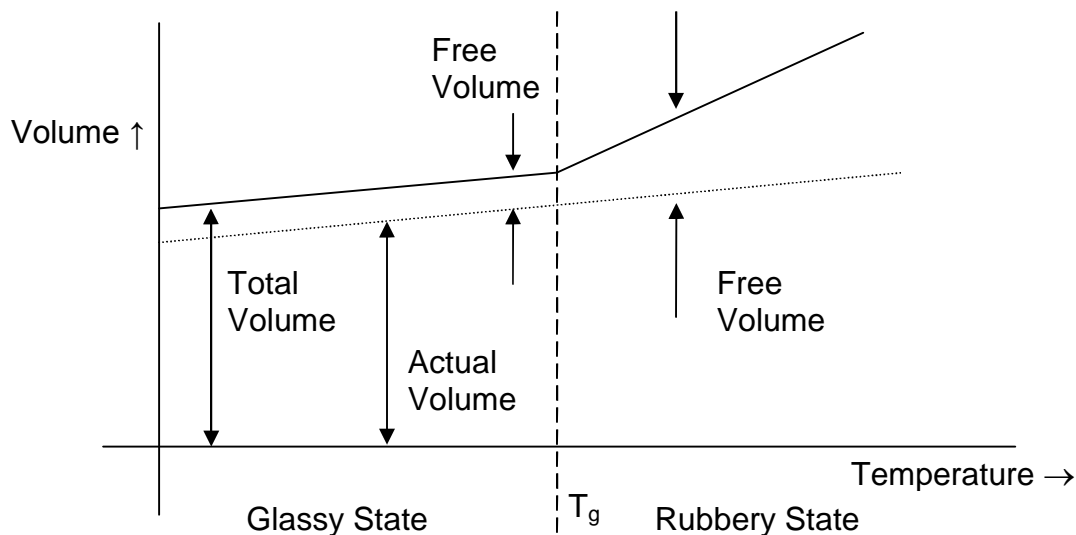
Figure 19 Graph to show free volume of polymers below and above T_g

Large increases of the free volume are present in the polymer if it is in the rubbery state at and above the T_g (Budd and McKeown, 2010). There appears to be a lack of consensus to the definition of free volume, but this concept has proved to be very useful in the explanation of the theory (Budd et al., 2005a, Ward and Sweeney, 2004, Seitz, 1993).

Thermal expansion is described as the expansion of the free volume in the polymer lattice when heat is applied. At atmospheric pressure, it is found that an empirical volume temperature relationship exists as shown in Equation 1, over a pressure range of $0.95 \leq \tilde{v} \leq 1.40$ quoted by Simha (Simha, 1977) reconfirmed by Rodgers and Consolati (Rodgers, 1993, Consolati, 2007).

Equation 1 Simha volume temperature relationship

$$Inv\ \tilde{v} = A + B\ ^{\sim}T^{\ 3/2}$$

Whereby:-

- $^{\sim}T$-temperature.
- A-0.10335 constant.
- B-23.8345 constant.
- $\tilde{v}$-volume.

Calculating the fractional free volume of a polymer in the glassy state is shown in Equation 2. Applying this equation the fractional free volume for amorphous polymers at the T_g is 2.5% (0.025 +/- 0.003) (Budd et al., 2005a, Ward and Sweeney, 2004).

Equation 2 Ward fractional free volume

$$f = f_g + \alpha_f\left(T - T_g\right)$$

Whereby:-

- f-fractional free volume.

- T-temperature.

- F_g-is the fractional free volume at T_g.

- αf-is the coefficient of expansion of the free volume, typically 4.8 x 10^{-4}.

A substantially larger free volume at or above T_g can be calculated from Simha and Boyer's relationship, as shown in Equation 3 (Simha and Boyer, 1962) and restated by Budd (Budd et al., 2005a).

Equation 3 Simha and Boyer's free volume

$$(\alpha_R - \alpha_G)T_g = 0.113 \ (11.3\%)$$

Whereby:-

- α_R-rubbery coefficient of thermal expansion.

- α_G-glassy coefficient of thermal expansion.

Table 12 shows experimental densities and free volumes of a range of different polymer types (Yampolskii et al., 2006).

Table 12 List of different polymers types with densities and free volume

Polymer	Density (g/cc)	Free Volume (%)
Poly trimethylsilyl propyne	0.75	27.7
Poly dimethyl phenylene oxide	1.066	7.4
Tetramethylhexafluorobisphenol PC	1.289	6.5
PC	1.164	3.2

Figure 20 shows an adapted graph of the free volume in PC which has a T_g of 147 $^{\circ}$C (Bohlen and Kirchheim, 2001) measured using positron annihilation lifetime spectroscopy (PALS). The free volume is the difference between the total volume (solid plot) and the actual solid volume (dotted plot). As the temperature increases the graph displays a constant free volume until T_g after which the free and specific volumes increase dramatically (Bohlen and Kirchheim, 2001).
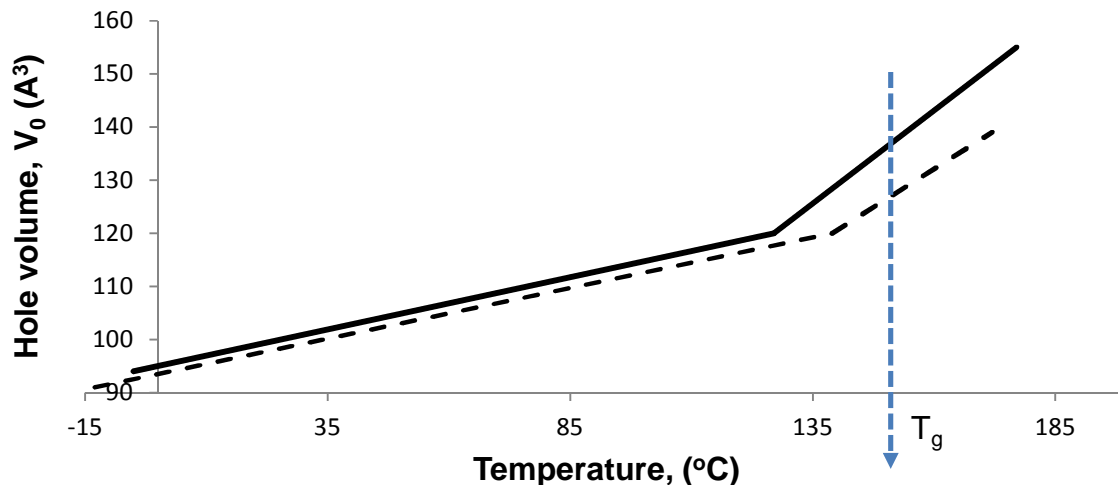
Figure 20 Graph of free volume in PC measured using PALS

The pressure, volume and temperature studies completed for PC establish a free volume content of 8-10% with an average hole size of 110A^3 at 37 $^{\circ}$C. Studies by Arnold and Bohlen, using PALS have found that PC has a free volume of 7-9% (Bohlen and Kirchheim, 2001, Arnold, 2010).

Dlubeck discovered by using PALS that PE has a free volume of 4.2% at T_g and 13.2% above T_g. The same study concluded that polytetrafluoroethylene has a free volume of 5.7% at T_g with a 13% free volume above T_g (Dlubek et al., 1998).

Semi-crystalline polymers such as polyethylene have amorphous and crystalline phases co-existing as a result free volume theories are not applicable. In these materials penetrants are considered to be insoluble in the crystallite regions of the polymer and diffusion only occurs in the amorphous phase (Lutzow et al., 1999).

In a semi-crystalline material it is believed that the amorphous regions supply the growing spherulites with polymer. This results in a permanent entanglement with the spherulites which leads to reduced movement of the polymer chains and eventually the crystal growth stops. Consequently the amorphous phase is presumed to be retarded, causing a reduction of free volume in this phase (Lutzow et al., 1999).

It can be assumed that the amorphous PC polymer has a free volume of 2.5% below T_g and 11.3% above (Budd et al., 2005a). The semi-crystalline PBT has a respective free volume of 1.5–1.6% below T_g and 6.78–7.34% above.

From the experiments it is evident that with both polymeric materials the free volume is sufficiently large enough when the material and process temperature is $\geq T_g$, facilitating dye penetration.

There are alternative methods in which the dye penetration can be explained, such as, Ficks law, osmosis and Brownian motion.

Ficks law (Fick 1855, Crank and Park 1968) illustrated in Equation 4, deals with the diffusion of permanent gases into and through polymers. There are two types of penetrant behaviour. The first is a low solubility of gas and concentration independent diffusion coefficients and a temperature and concentration independent energy (Crank and Park 1968). The second is with larger vapour molecules characterised by non dilute penetration polymer mixture, marked concentration dependant diffusion coefficients and temperature dependant energies of activation (Crank and Park 1968).

Equation 4 Ficks law

$$J=-D*(\Delta C/\Delta x)$$

Whereby:-

- J= flux
- C=concentration

- x=distance
- D=diffusivity

Osmosis is when two solutions of different concentration types and are separated by a membrane which is permeable by the smaller solvent molecules but not to the larger ones, then the solvent will tend to diffuse through the membrane from the less concentrated to a more concentrated solution (Cheryan 1998).

Brownian motion can be described by the motion of a particle suspended in a viscous fluid resulting from fluctuating forces which are the consequence of collisions with adjacent molecules of the fluid. The details of Brownian movement cannot be predicted exactly however it is assumed that collisions and displacements are random. Therefore even though the precise details of the phenomenon are unknown, the average behaviour can be determined. In a suspension all the particles undergo Brownian motion and therefore particles will tend to flow from regions of high concentration to ones with low concentration. This flow is termed diffusion and it causes the concentration of a suspension to become uniform (Brown, 1827, Brinkman, 1956).

These three established principles are relevant to the diffusion of gasses into polymers but cannot be readily applied to the dye sublimation process. The dyes used in the process are considered not to be permanent gases, they are only in gas form when heat is applied and when cooled they condensate back into a solid material. Therefore these principles are not considered to be the mechanism whereby the dye penetrates the polymer surface.

5.2.5.1. FURTHER EXPERIMENTATION USING FREE VOLUME

It is hypothesised here that the free volume present in the polymer is a significant contributing factor to the level of dye penetration into the substrate. To understand the practical impact of the free volume in polymers, additional experimentation was undertaken. This involved taking a pre-decorated PBT substrate and re-exposing it to heat. The intention was to verify if the increased free volume of the heated specimen allowed further transportation of the dyes into the polymer.

Table 13 PBT Free volume dye penetration experimentation

Temperature (^{o}C)	Average dye penetration depth (μm)				Average
	C	**M**	**Y**	**K**	
Starting dye penetration	-	-	-	-	**28.27**
69	47.71	53.63	54.18	46.49	50.50
114	305.86	315.48	307.84	289.2	304.60
159	372.02	572.9	490.72	594.71	507.59

The experiment was undertaken on three specimens of pre-decorated PBT, processed at 180 ^{o}C, 20 seconds, this specimen had a level of dye penetration measured to be 28.27 μm. Three different temperatures were used for these experiments 69 ^{o}C (T$_g$ +20 ^{o}C) 159 ^{o}C (T$_g$ +110 ^{o}C) and a midpoint of 114 ^{o}C, all of the specimens were exposed to these heats for 240 minutes. Five dye penetration measurements were taken for each colour, the average results are shown in Table 13 further details can be found in **portfolio submission 3**.

The results illustrate that by increasing the temperature to 69 ^{o}C, the free volume has increased sufficiently enabling the dyes to migrate further into the polymer by a factor of 1.8. By exposing the specimen to 159 ^{o}C, the dye penetration depth has increased by a factor of 18. The improved level of dye penetration is three times more than previously recorded during any of the original dye sublimation experimentation.

The experiments described in section 3.2.3 and the results in section 4.3 highlight that the dyes sublimate between 119-210 ^{o}C. Therefore at the experimental temperatures, 69 and 114 ^{o}C the dyes are not sublimating and the increase in the dye penetration depth is solely the result of the free volume increasing and interconnecting sufficiently enabling improved dye penetration. It is not thought or has been reported that the dyes are re-sublimating at 159 ^{o}C during the experimentation (Cobb, 2010).

This experimentation assumes that an isothermal condition is achieved in the polymer substrate. However this may not be the case at all sublimation printing process settings and further investigation would be required to establish if the substrate is isothermal or if a thermal gradient exists in the specimen.

5.2.6. THE DYE DEPTH PENETRATION MEASUREMENT ERRORS

As discussed in sections 5.2.1 and 5.2.2 there were errors in the measurement results from the experimentation completed in section 3.2.2. This section discusses how the author believes the errors came about. The variation noted in the dye penetration measurements was more evident at the higher processing temperatures. The measurement errors were due to manual error and the difficulty in establishing where the level of dye penetration finished in the polymer.
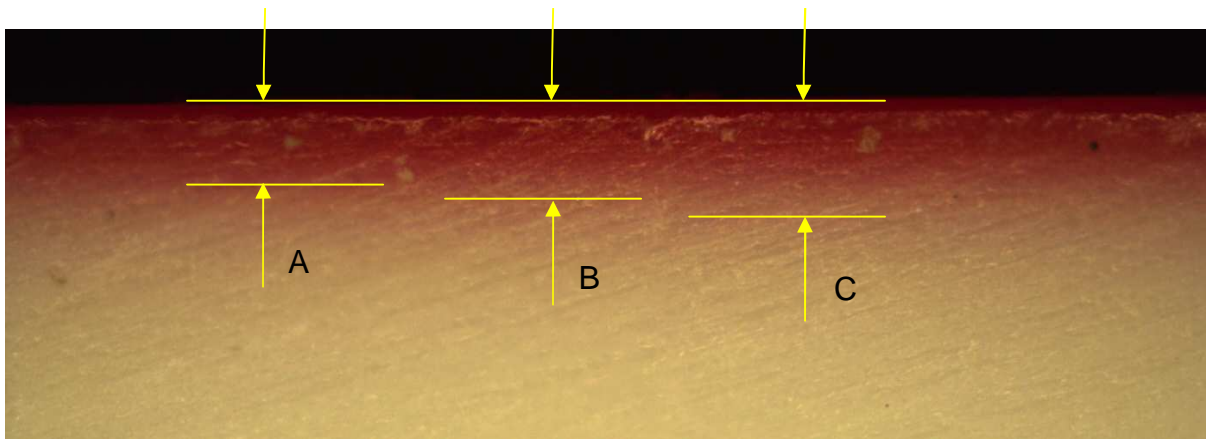
Figure 21 PBT with "M" dye displaying the measurement difficulty

Figure 21 shows an image from the optical microscopy of PBT decorated using the "M" dye three possible measurement points are shown as A, B and C. These three end points vary approximately 10 μm. This demonstrates the difficulty in trying to establish where the dye ceases penetration. Measurements were taken using a consistent approach to gain a level of reliability with the data. In all cases the author used point B.

At the lower temperatures the level of measurement error was far less as the dye had penetrated to a more defined end point, as seen in Figure 22. In this case any variations present are more likely to be the result of dye penetration variability and less so measurement error. The author proposes an investigation to find an alternative and more reliable method of measuring the dye penetration depth in a polymer substrate, in section 10.
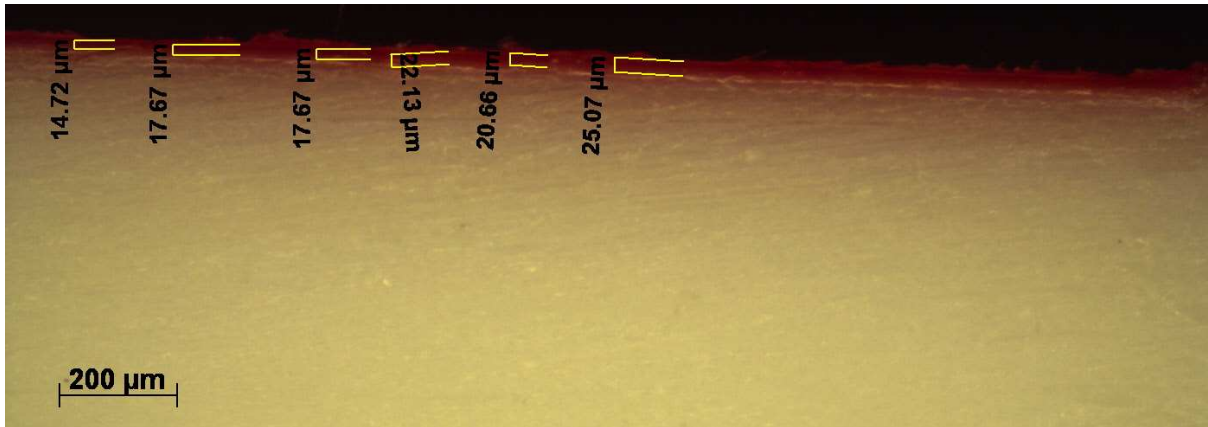
Figure 22 PBT with "M" dye at 160 °C

5.2.7. VISUAL APPRAISAL OF THE SUBSTRATE DECORATION

The following section appraises the decorated image quality of the PC and PBT substrates, the decorated specimens objectively appraised by the author; the results are shown in Table 14.

Table 14 Visual appraisals of PC and PBT decorated substrates

Polymer	Temperature (°C)	Time (seconds)			
		20	40	60	80
PC	140	F	F	F	F
	160	F	F	F	OK
	180	OK	OK	OK	B
	200	OK	B	B	B
PBT	140	F	F	F	F
	160	F	F	F	OK
	180	OK	OK	OK	OK
	200	OK	OK	OK	B

Whereby:-

- F-feint image.
- B-blurry image.
- OK-acceptable.

Figure 23 displays photographs of the decorated PC substrates at the different temperatures with the time shown from left to right, 20-80 seconds. The faint images recorded in Table 14 are the result of insufficient transfer of the dyes into the surface of the PC. It is noted that at 140 ^{o}C there is insufficient coverage of the dyes on the surface of the substrate.
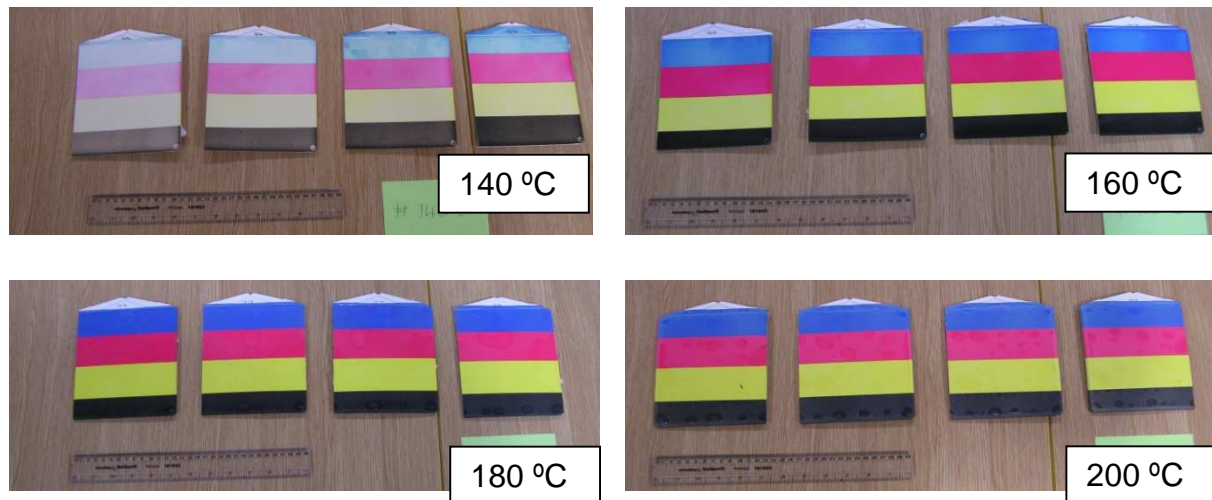
Figure 23 PC Photographs of the decorated substrates at 140 - 200 ^{o}C

Figure 24 shows an image of the surface of the decorated PC, it shows a very faint background with spots of colour which are more prominent where dye transfer has started to occur. This could be very similar to the condition as report by DuPont (Anon, 2005) where the dye is reported to scratch off easily.
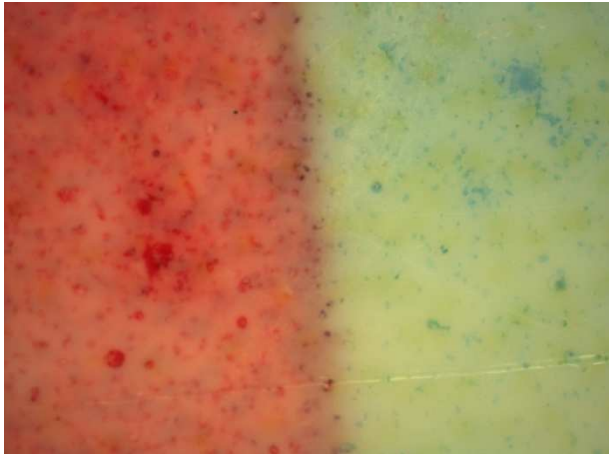
Figure 24 PC Photograph of the surface showing a "faint" decoration
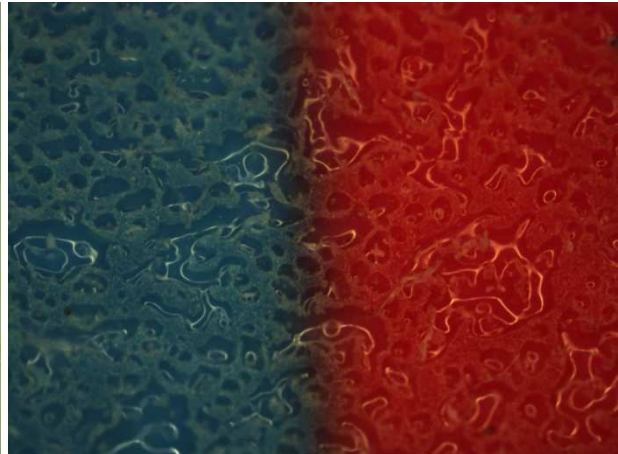
Figure 25 PC Photograph of the surface showing a "blurry" decoration

Figure 25 shows a photograph of the decorated PC surface, a high level of blurriness is witnessed instead of a defined intersection between the two colours. This is the result of the substrates being processed at 180 °C, 80 seconds and 200 °C, 40-80 seconds.
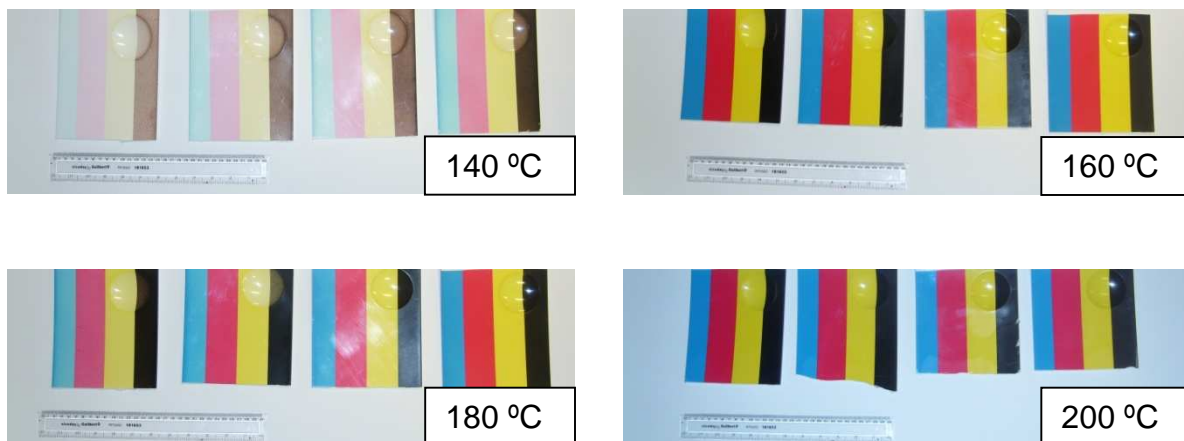
Figure 26 PBT Photographs of the decorated substrates at 140 -200 °C

Figure 26 shows photographs of the PBT printed substrates. The process times run from 20-80 seconds, from left to right. The results in Table 14 show that at 140 °C, 20-80 seconds and 160 °C, 20-60 seconds the decorated surfaces were too faint, as shown in Figure 27.
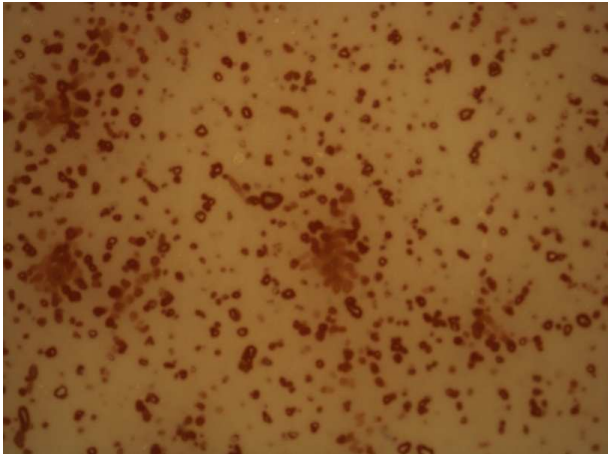
Figure 27 PBT Photograph of a faint decorated surface

At 180 ^{o}C, 20-80 seconds and 200 ^{o}C, 20-60 seconds all of the decorated surfaces were acceptable. At 200 ^{o}C, 80 seconds the image was too blurry, this was due to an excessive amount of free volume in the PBT causing the different coloured dyes to diffuse into each other using the polymer as a transport medium.

It must be considered that the dyes penetrate the polymer in "all directions". As revealed dye penetration occurs into the polymer substrate as a result of the free volume. This enables the dyes to move across boundaries causing the image to blur when compared to the original condition.

Figure 27 shows the faint image of the decoration on the surface of the polymer however dark "pixels" of the dye are evident amongst a very faint background. It appears that as the dyes are sublimating they nucleate from random pixels which grow. As more pixels sublimate and the polymer free volume increases they interconnect sufficiently to evenly cover the surface of the polymer. These random pixels are from the printed transfer carrier where the dyes have started to sublimate earlier than others.

5.2.8. VISUAL APPRAISAL OF THE SUBSTRATE SURFACE

Following decoration of the PC specimens, it was evident that some had suffered thermal damage to their surface; due to the heat applied during the decoration causing the polymer to become liquid, this section describes the cause of this condition.

For the PC substrates surface, thermal damage is evident when they are processed at 180 $^{\circ}$C, 60–80 seconds and at 200 $^{\circ}$C, 20-80 seconds. At 140–160 $^{\circ}$C and 180 $^{\circ}$C, 20–40 seconds there is no evidence of thermal damage to the specimen surface.

Figure 28 PC Photograph of the surface showing thermal damage

Figure 29 PC Photograph of the surface showing no thermal damage

Figure 28 shows an image of the decorated PC specimen, processed at 200 $^{\circ}$C, 60 seconds; it clearly shows inconsistencies to the surface structure as a result of thermal damage. Figure 29 shows a PC specimen processed at 160 $^{\circ}$C, 80 seconds, where there is no thermal damage to the surface of the polymer.

The visual appraisal of the PBT showed no thermal damage to the specimens at any of the process settings.

The decorated condition of both polymers highlighted limitations for the PC to be used in the dye sublimation process at elevated temperatures, whilst the PBT coped extremely well throughout the experimental temperature range.

Semi-crystalline polymers such as the PBT have two thermal "milestones" to be considered, the first is the T_g. When the polymer is exposed to a temperature below this point the molecules become immobile, giving it a glassy nature. The second milestone is the melt transition temperature (T_m) when the temperature is above this point the polymer is determined to be fully molten, in a liquid phase. Between the T_g and T_m the polymer is known as being in a rubbery phase (Hatakeyama and Quinn, 1999, Mark, 2007).

The T_g of the PC and PBT and the T_m of the PBT was established using a Triton Technologies, Tritec 2000, Dynamic Mechanical Thermal Analyser (DMTA) this a recognised technique for determining the T_g and T_m of polymers (Hatakeyama and Quinn, 1999, Keating, 1998). The polymers were evaluated using a 25-250 ^{o}C temperature range at a ramp rate of 10 ^{o}C/min, using a single cantilever arrangement.

Figure 30 shows a graph of the DMTA results for the PC, temperature is shown on the x-axis and modulus is shown on the y-axis. For this grade of PC the onset of T_g is 132 ^{o}C and the polymer becomes fully liquid at 163 ^{o}C.
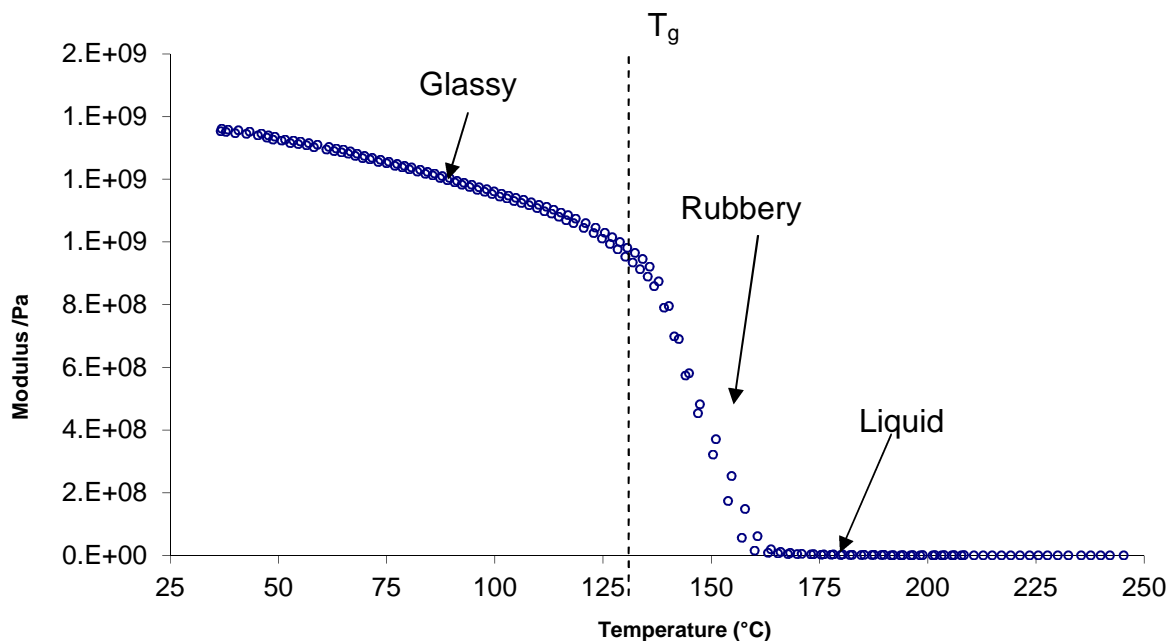
Figure 30 PC Graph of DMTA results

Figure 31 shows the DMTA results for the PBT polymer, for this grade of PBT the T_g is 49 ^{o}C and the T_m is 203 ^{o}C, after which the polymer has become liquid.
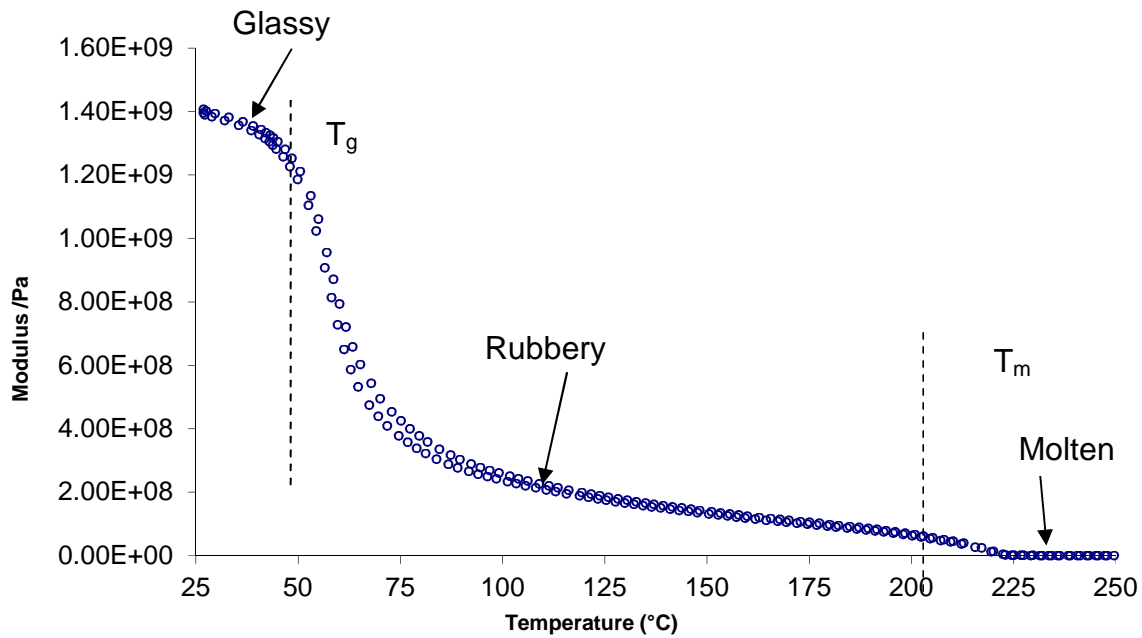
Figure 31 PBT Graph of DMTA results

The DMTA results show that the T_g of the PBT is lower than recorded for the PC, a difference of 83 ^{o}C is noted. Beyond the T_g the PBT remains rubbery until the T_m is reached at 203 ^{o}C. The ability for the PBT to remain in a rubbery state during the dye sublimation experiments has enabled it to survive thermal damage.

5.2.9. SECTION CONCLUSIONS

The experiments have highlighted a number of points for the performance of dye penetration with both amorphous and semi-crystalline polymer types. The methodologies for the experimental set up and substrate evaluation proved to be reliable.

Adams reported that 5 µm can be added to the thickness of a PC substrate (Adams, 2007) from the experiments this condition appears to be improbable. However without knowing the actual materials and process used in determining these measurement values it was difficult to replicate this condition.

All of the samples from the experiments showed only dye penetration. The PBT polymer is reported to have a dye penetration of 200 µm (Adams, 2007). This situation was not recreated but achieving this depth is more probable. Through calculations it was established that using a temperature of 200 ^{o}C and 111 seconds this depth could be achieved. Differences were noted with regards to CMYK dye penetration however these were deemed as being minor and could not explain the differences in the published and experimental results.

Experimentation shows that the dye penetration depth between PC and PBT is very similar. At 140, 160 and 180 ^{o}C the average dye penetration depths are 6, 17 and 52 µm for both materials respectively suggesting that the percentage free volume penetrated by the dye to be similar. The PBT has an improved level of dye penetration at 200 ^{o}C as it has survived the processing temperature. Further experimentation highlighted that the aesthetic condition of the decoration and substrate surface should also be taken into account.

"DuPont does not share information regarding the crystallinity and free volume of their polymer materials" (Coates, 2010). However the degree of crystallinity is generally quoted to be 35-40%, for PBT polymers (Fakirov, 2005). It is unclear if this is representative for the grade of PBT selected for these experiments but it can be treated as a reasonable guide. This means that the PBT polymer will have an amorphous level of 60-65% containing free volume.

It can be assumed that the amorphous PC polymer has a free volume of 2.5% below T_g and 11.3% above (Budd et al., 2005a). The semi-crystalline PBT has a free volume of 1.5–1.6% below T_g and 6.78–7.34% above, the results show that this reduced level is not restrictive to the level of dye penetration. The experiments demonstrate that with both polymers the free volume is sufficiently large enough when the process temperature is $\geq T_g$.

The rate of dye penetration is comparable for the PBT and PC polymers at 140–180 ^{o}C, however the rate of penetration has increased by 58% for PBT at 200 ^{o}C. This is due to the ability of the PBT to thermally survive at the higher process temperature, allowing the free volume to be increased. This is despite the reduced level of available free volume. The errors in the dye penetration measurements rise as the process temperature and resulting free volume is increased, this is because the free volume causes the dye to penetrate further in an almost uninhibited manner, leading to the variability in the level of measured dye penetration.

At 200 ^{o}C the PC achieves a dye penetration depth of 94 µm and the PBT achieves a greater level at 154 µm, for this condition the temperature of the polymer must be sufficiently high. The T_g of the PC is 132 ^{o}C after which the polymer becomes rubbery, at 163 ^{o}C it is in a liquid state. At this high temperature the polymer is not suitable for decoration, as the polymer is in a liquid state. In this condition the polymer is unable to hold a shape however the free volume is considered to be at its greatest.
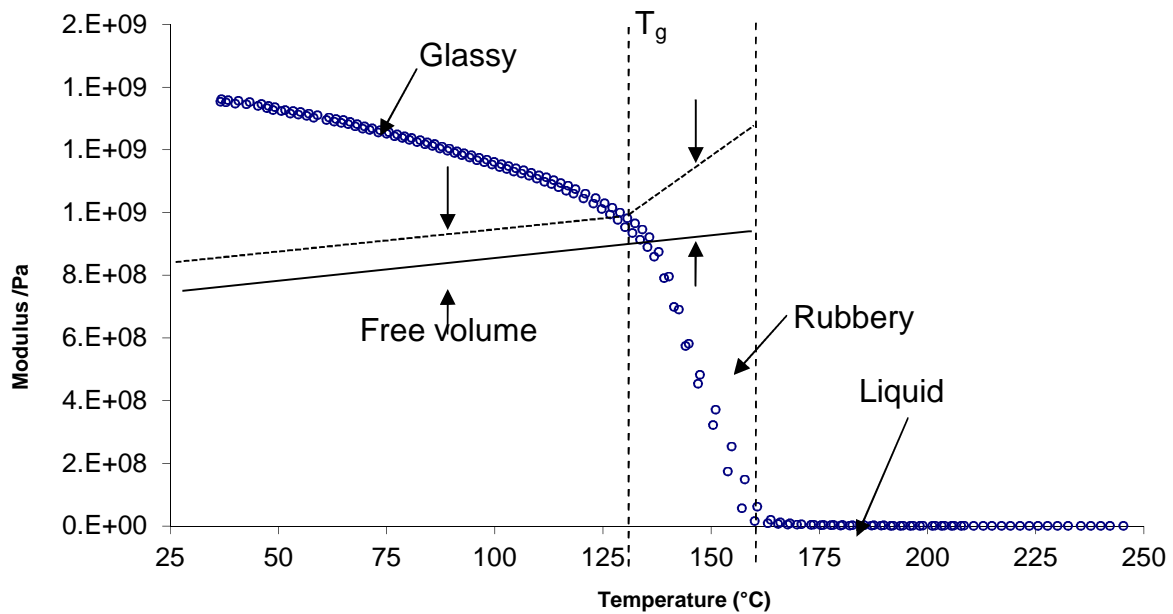
Figure 32 PC Free volume overlaid onto the T$_g$

For PC the ideal processing temperature for the dyes to penetrate into the polymer is between the T$_g$ and the point at which it becomes liquid, providing a very narrow window to operate the process.

A graph depicting the free volume between the solid and dashed line, in relation to the T$_g$ and liquid condition is shown in Figure 32. The graph shows that the free volume is constant until the T$_g$ is reached at 132 °C. At T$_g$ the free volume increases but this is only until the polymer becomes liquid at 163 °C.

For the PBT at the elevated temperature the free volume is "active" and for a longer temperature range during the process, enabling the free volume to expand and the dye to penetrate more readily. This is depicted in Figure 33 where the free volume between the solid and dashed line has a larger temperature range to expand from T$_g$ 49 °C before the polymer becomes fully molten at T$_m$ 203 °C.
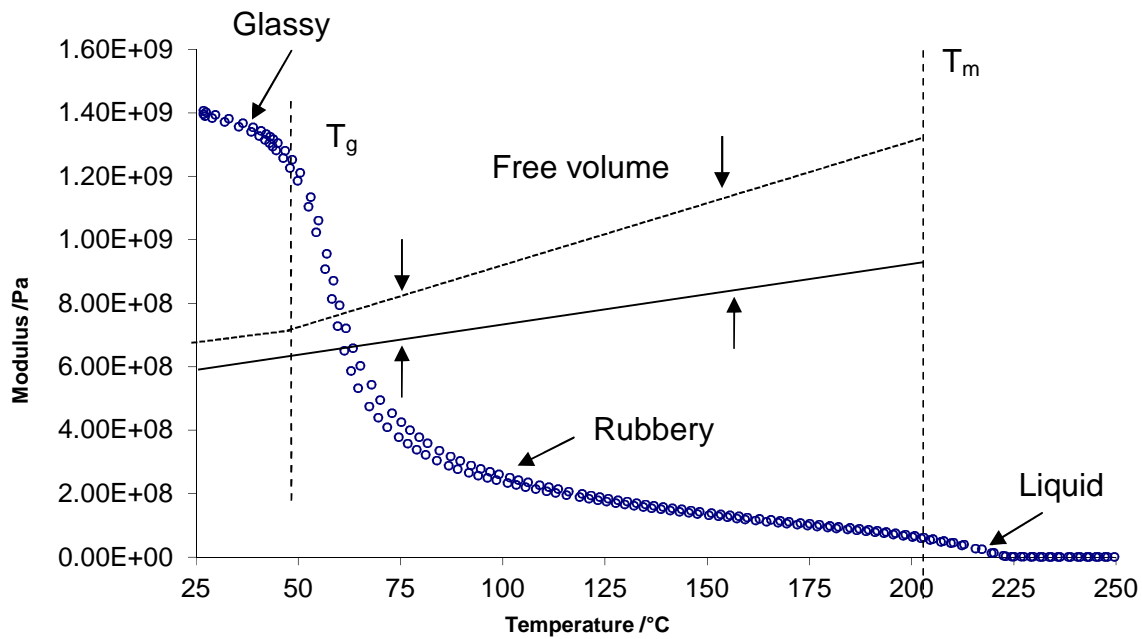
Figure 33 PBT Free volume overlaid between the T$_g$ and T$_m$

The free volume appears to be the fundamental mechanism for allowing the dyes to penetrate the polymer surface. This was validated by the further free volume experimentation. Increasing the temperature and the free volume in a decorated PBT component enabled further penetration of the dye into the polymer surface. This technique could be used to commercially exploit improved dye penetration depth in a polymer.

The component can be decorated using a short time, subsequently it can be placed into an oven at a temperature above the T$_g$ of the polymer, which can be used to increase the free volume and enable further dye penetration. This process can be achieved in a very simple and inexpensive oven, away from the more costly transfer press.

Processing amorphous polymers at or above the T$_g$ would ensure sufficient dye is penetrating the polymer, however the temperature at which the polymer becomes liquid would need to be avoided. For semi-crystalline polymers processing above the T$_g$ and as close to the T$_m$ as possible, would be recommended. This would achieve the highest level of free volume in the polymer therefore facilitating the greatest level of dye penetration.

The dye sublimation processing time is significant as this enables the polymer to become isothermal and achieve a uniform free volume condition through the bulk of the polymer material. Higher processing times lead to higher levels of dye penetration.

Another important finding from this research is the criticality of the T_g for polymer with respect to operating temperature of a decorated component. If the T_g of a polymer is below room temperature, e.g. polypropylene T_g 0~13 ^{o}C (Mark, 2007) the dyes will continue to move through the free volume in the polymer without interruption. This would cause the quality of a decorated image on the surface of a component to degrade and blur. Therefore it would be recommended that the material selection criteria should take into account the T_g of the polymer and the environmental temperature the decorated component will be used in. Using a polymer with a sufficiently high T_g will ensure that during daily use of a decorated component the free volume is minimised and dye migration in the polymer is sufficiently restricted.

For both polymer types the highest rate of penetration occurs at the high processing temperature of 200 ^{o}C. Throughout the temperature range the highest rate of penetration occurs during the first 20 seconds of processing time. However for PBT the rate of penetration is very similar when the polymer processed at 20–40, 40-60 and 60–80 seconds. This suggests that the penetration rate is similar due to the enlarged free volume condition of the polymer.

The different CMYK dyes penetrate the PBT polymer with a 4 µm range across all process temperatures and times, the range for the PC is 6 µm. The results show that the different CMYK colours penetrate the polymer to similar depths. Although individual colours are identified as being the deepest and shallowest to penetrate the polymers, the reality that they penetrate the polymer to similar depths with an acceptable level of variance is relevant. In the majority of instances the printed colour pallet is generated by using the CMYK mixed together (Bamberg, 2005).

No factors within the process identify a method of enabling any of the CMYK to penetrate more or less.

Table 15 PC& PBT Acceptable process settings and dye penetration depths

Polymer	Temperature (°C)	Time (seconds)			
		20	**40**	**60**	**80**
PC	140	-	-	-	-
	160	-	-	-	OK (19.51)
	180	OK (43.31)	OK (48.24)	-	-
	200	-	-	-	-
PBT	140	-	-	-	-
	160	-	-	-	OK (26.64)
	180	OK (28.26)	OK (37.07)	OK (60.31)	OK (86.86)
	200	OK (131.95)	OK (150.05)	OK (157.43)	-

Table 15 shows the processing data and dye penetration depths for PC and PBT, whereby an acceptable component can be produced when considering the aesthetic and surface condition of the decorated substrate. The table illustrates a larger range of processing parameters for PBT when compared to the PC. Using the settings highlighted would produce components with an acceptable decoration on the surface with no thermal damage. Using the other settings would produce undesirable components. The process at 160 °C, 80 seconds does not achieve a level of penetration that would be comparable to the thickness of a paint film or IMD surface. However 19.51 µm of dye penetration is an acceptable level and should not be discounted.

6. ANALYSIS AND DISCUSSION OF THE DYE THERMAL CHARACTERISATION

The following section analyses and discusses the results of the DSC experimentation shown in section 4.3.

For the "C" dye material, the results show that T_{P1} and T_{P2} occur at the lowest temperature compared to the other dyes. The results also show that the "Y" dye material has the greatest water content of the different dyes. The results show that for the "M" dye T_{P1} occurs at the greatest temperature and T_{P2} is the second highest, compared to the other dye materials, the range for this dye is 63 ^{o}C, whereby the dye material can sublimate.

The "Y" dye material has the second lowest temperature for T_{P1} and the lowest temperature range between T_{P1} and T_{P2} at 52.8 ^{o}C, providing a narrow temperature range for the dye material to sublimate. This colour dye material has a high level of water content similar to the "C" dye material, which again relates to the low temperature performance of the sublimation. The enthalpy value for this colour is significantly higher when compared to the other colours.

The "K" coloured dye has the second highest T_{P1} temperature and the highest temperature of T_{P2}. The range between T_{P1} and T_{P2} is 68.3 ^{o}C this is the largest compared to the other dyes enabling a large window of the dye sublimation. This colour has the lowest level of water content at 55% which indicates that the composition could contain more dye enabling a higher sublimation temperature.

Figure 34 shows a graph of T_{P1} and T_{P2} for all of the dyes materials, plotted together with the water content displayed in Table 8. The graph shows a clear relationship between the moisture content and the thermal transitions of T_{P1} and T_{P2}. It is noted that higher water content in the dyes results in lower thermal transition temperatures of T_{P1} and T_{P2}, notably with the "C" and "Y" colours. It could be likely that these colours contain less of the actual dye component or have a smaller molecular size compared to the "M" and "Y" colours, but this has not been established through this research.
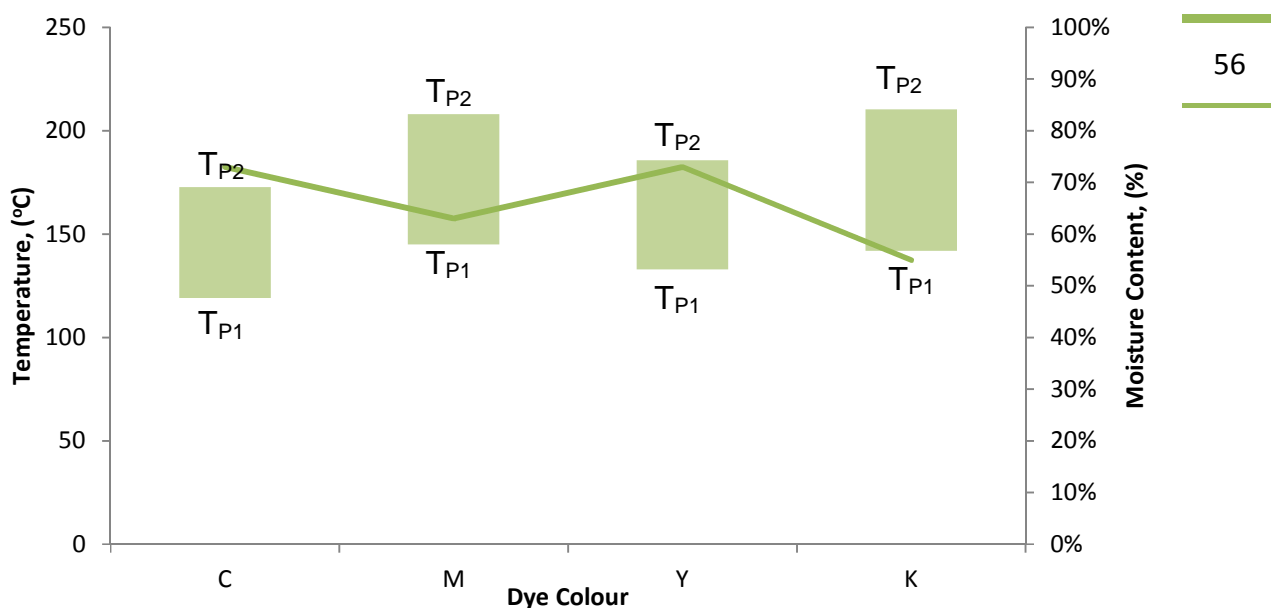
Figure 34 T$_{P1}$ and T$_{P2}$, plotted with the water content for all colours

Inkjet dyes are based in a water solution to enable them to flow in the printer (Meyer, 1975, Lee, 2005). With the "C" and "Y" dyes it is established that the dye material has more water in the formulation and less of the DEG and glycerine. The DEG is used to disperse the dye in the composition (Chavan and Jain, 1988) and the glycerine acts as a solvent (Leffingwell et al., 1945). Additionally the DEG and glycerine act as humectants (Yoon and Choi, 2008). They prevent the dyes from drying out which would cause inkjet nozzle blockages and result in poor quality printing (Gregory, 1991).

The higher water level for the "C" and "Y" dyes leads the author to believe that the DEG and glycerine are used in lower quantities compared to the "M" and "K" specimens. The "M" and "K" dye compositions may be prone to inkjet nozzle blockages and therefore higher quantities of humectants are required in the formulation. This may be due to the larger molecular size of the dyes (Burknishaw, 1995); however this avenue of research is beyond the scope of this work. Figure 34 illustrates the higher quantity of the DEG and glycerine enables "M" and "K" to have higher T$_{P1}$ and T$_{P2}$ temperatures. DEG has a boiling point of 240-250 ^{o}C (Flick, 1998, Grause et al., 2004) and glycerine has a boiling point of 290 ^{o}C (Pagliaro and Rossi, 2010). These colours have a 10–15 ^{o}C larger processing range compared to the "C" and "Y" colours, allowing for a greater range that the dye materials can sublimate in.

Figure 35 illustrates a plot of the thermal transitions for all of the CMYK colours; the range between the highest and lowest values is shown. The graph shows that at the start of sublimation, T_{P1}, the temperature is 119 ^{o}C, with a range of 26 ^{o}C, at the end of sublimation T_{P2} the temperature is 172.7 ^{o}C with a range of 37 ^{o}C.
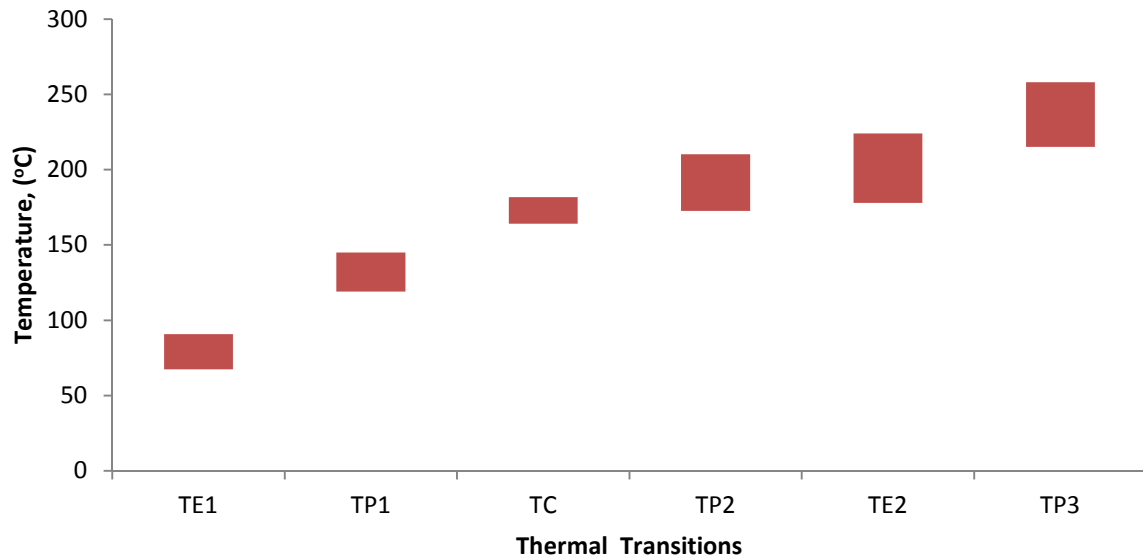
Figure 35 Thermal transitions and ranges of the dye materials

These temperatures are highlighted in Table 8 as the "ideal" temperatures for T_{P1} and T_{P2}. The results suggest that the process should be operated at the maximum thermal transition temperature for T_{P1} and T_{P2} to ensure all of the CMYK dyes are fully sublimated during the process, they would normally be printed together.

Where the polymer substrate allows, it must be considered that the greatest amount of sublimation occurs between T_C and T_{P2}; the dye sublimation user should ideally consider processing between 181.8-210 ^{o}C. The experimentation detailed in section 5.2.8 highlighted that the PC is liquid at this temperature but the PBT is in the "ideal" rubbery condition.

Transition T_{P3}, occurs in a range 215–258 ^{o}C, with an average value of 243.5 ^{o}C. This is considered to be the boiling of DEG which has a boiling range 240–250 ^{o}C established by Flick and Grause (Flick, 1998, Grause et al., 2004). It is not thought that the peak at T_{P3} is glycerine which has a boiling temperature of 290 ^{o}C (Pagliaro and Rossi, 2010).

DEG is commercially used to chemically break down Polyethylene terephthalate (PET) in a process commonly known as glycolysis (Scheirs and Kaminsky, 2006, Pardal and Tersac, 2006). This process is becoming increasingly popular as the worldwide consumption of PET drinking bottles is increasing, so polymer recycling or oligomer recovery becomes ever more crucial (Pardal and Tersac, 2006). Although a great deal of the research for glycolysis generally occurs with commercially prevalent PET, the process can also be used on PBT (Rajesh and Ramesh, 2002). The process can use DEG, ethylene glycol, di-propylene glycol or glycerol to chemically cleave the polymer resulting in ethylene glycol. Studies completed by Pardal (Pardal and Tersac, 2006) reveal that DEG at 220 ^{o}C is highly effective at breaking down PET into ethylene glycol, compared to other glycol types.

During the dye sublimation process the DEG could potentially chemically attack the PBT surface being decorated. This could be further aggravated if the printed image use a high level of the "M" and "K" colours as these were highlighted to contain more DEG. T_{P3} for "C" is lower than the other colours tested at 215 ^{o}C, this could be the result of a lower DEG content or a different grade used in the composition by Sawgrass. To avoid chemically breaking down the PBT substrate, the user of the process should be using the lowest processing temperature, whilst still achieving the desired dye penetration depth as established in section 3.3. During analysis of the decorated substrates the author did not witness any evidence of degradation.

The ramp rate experiments described in section 3.2.3, completed on the "Y" dye colour reveal that as the heating rate increases, so does the reaction kinetics. This is the expected result when DSC ramp rates are increased (Hatakeyama and Quinn, 1999) the results show that the trend for T_{P1} and T_{P2} both increase as the ramp rate increases, as observed in Figure 36. This is a characteristic chemical reaction of the material used in the experiments (Williams, 2011).

However for T_{P3}, as the ramp rate is increased, the temperature peak remains comparatively stable. This shows that the reaction occurring at this temperature peak is a physical change to the DEG (Williams, 2011).
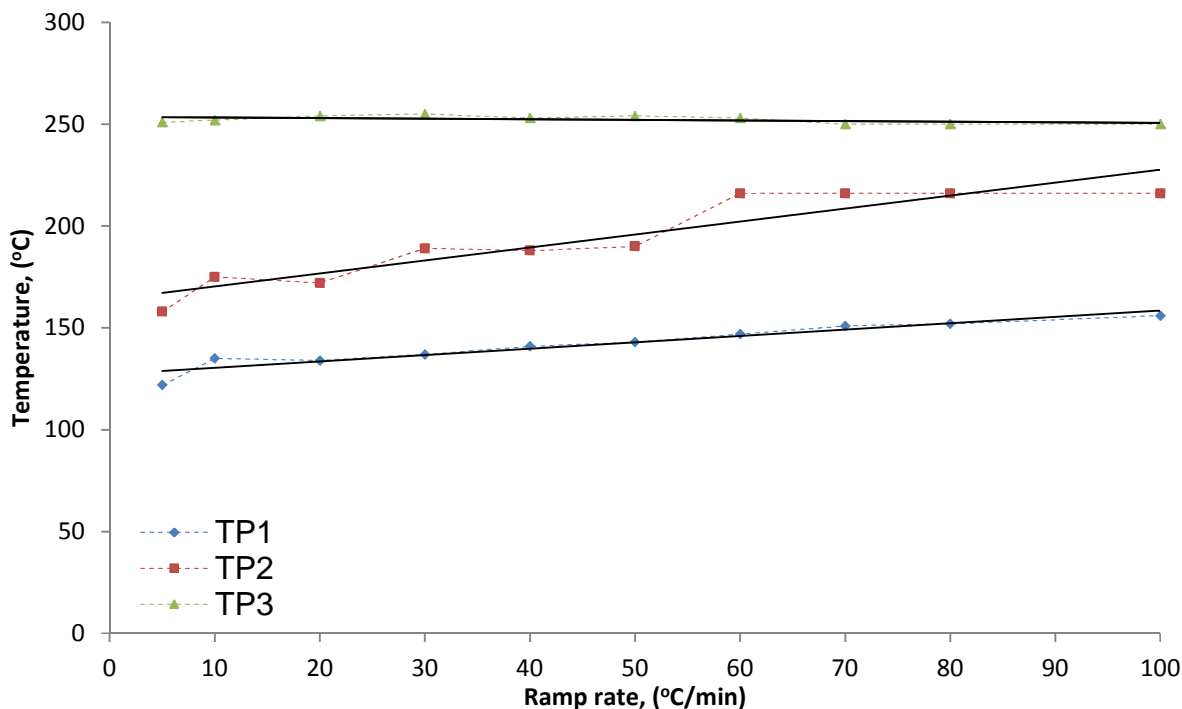
Figure 36 Plot of increased ramp rates for the "Y" dye material

6.1. SECTION CONCLUSIONS

The DSC experimentation identifies the usefulness of the technique to establish the sublimation characteristics of the dye materials. The experimentation identifies that CMYK dyes start sublimation at different temperatures, T_{P1} 119-145 ^{o}C , however as all of the colours are printed together, it must be considered that the minimum sublimation temperatures is 145 ^{o}C and the maximum is 210 ^{o}C. This was visually confirmed by experimenting using dye materials in the oven.

Figure 37 shows the average of all of the DSC results, plotted on the primary y-axis. The average dye penetration results for PC and PBT are plotted on the secondary y-axis, established in **portfolio submission 3,** both results are plotted against temperature. The results illustrate an excellent correlation between dye penetration and sublimation between T_{P1} and T_{P2}. The greatest level of dye penetration is evident at T_{P2}, when the dyes have fully sublimated, coinciding with the maximum available free volume of the polymer substrate at the processing temperature.
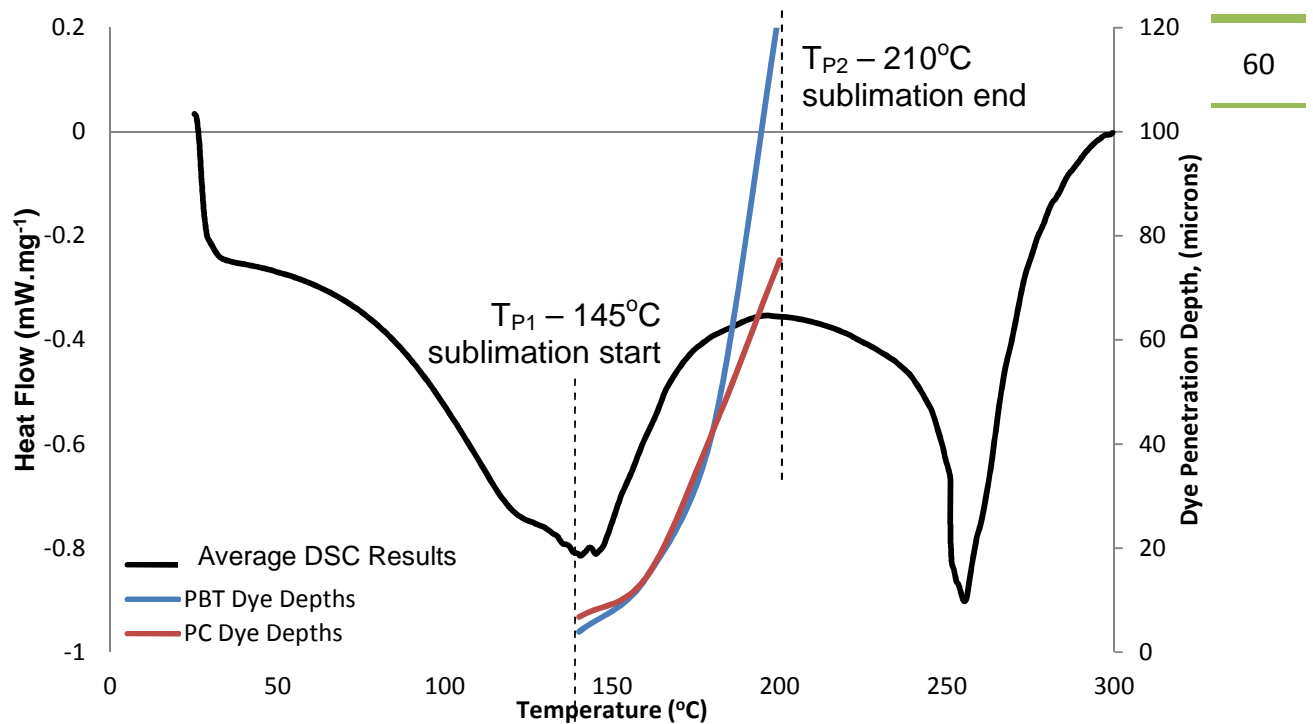
Figure 37 Average DSC results and average dye penetration depths PC & PBT

The DSC results imply that amorphous polymers should have a $T_g \geq T_{P1}$ of the dye materials. Ensuring the substrate polymers are able to withstand the high processing temperature and the dye materials have commenced sublimation. The temperature at which the polymer is fully liquid needs to be high enough to enable the dye materials to sublimate into the maximum free volume the polymer can achieve.

Figure 38 shows the average DSC results for the dye materials plotted on the primary y-axis with the DMTA results for PC plotted on the secondary y-axis, both results are plotted against temperature. The plots illustrate that at the temperature when the polymer becomes rubbery the dye material is sublimating and only a small thermal processing range exists, before the polymer becomes fully liquid. Considering these results the highest temperature at which the process should be operated is 160 ^{o}C.
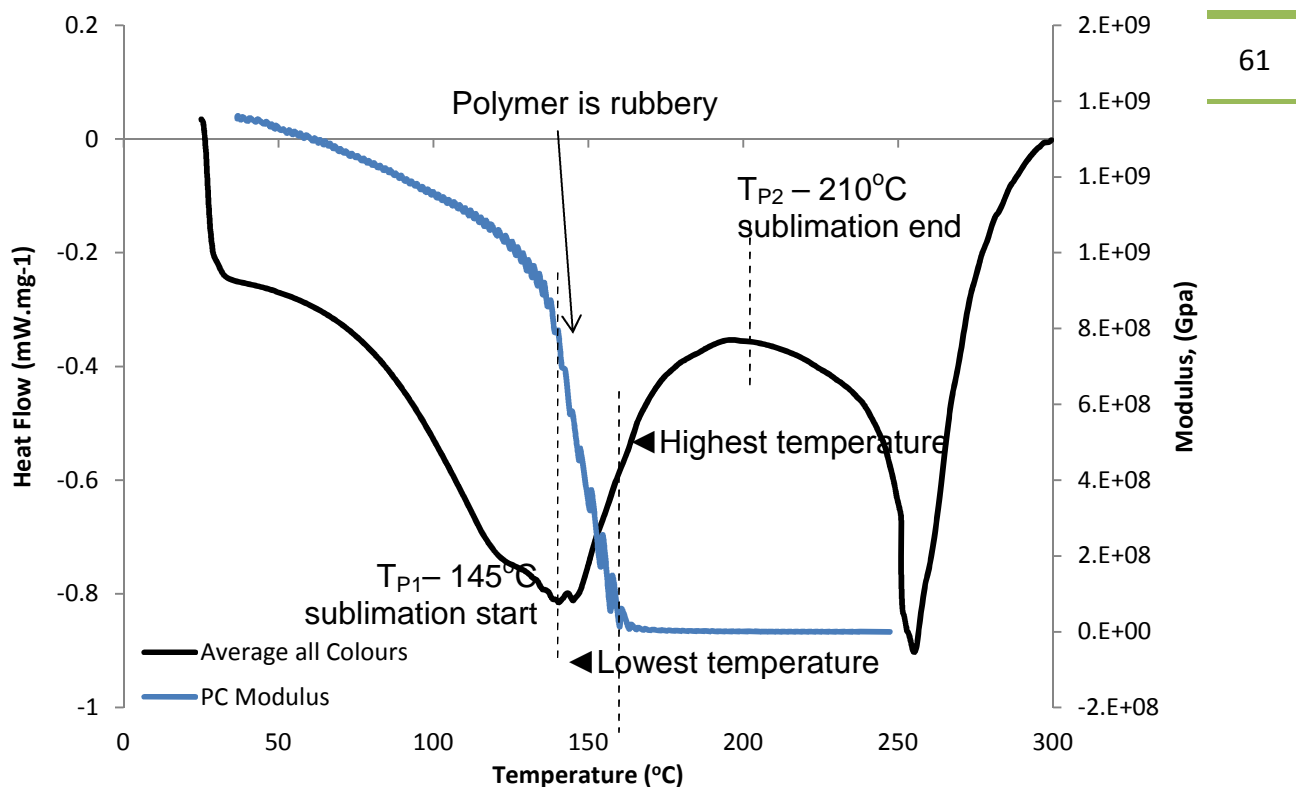
Figure 38 Average DSC results plotted with the DMTA results of PC

Semi-crystalline polymers ideally need to have a $T_g \leq T_{P1}$ to ensure that the free volume has increased prior to the dye material sublimating. Ideally the polymer should have a $T_m \geq T_{P2}$ of the dye materials, ensuring that it is in a rubbery condition, enabling the sublimated dyes to penetrate the enlarged free volume.

A graph of the DMTA results for the PBT and the DSC results of the dye materials is shown in Figure 39, highlighting the lowest and highest processing temperature for this material type.
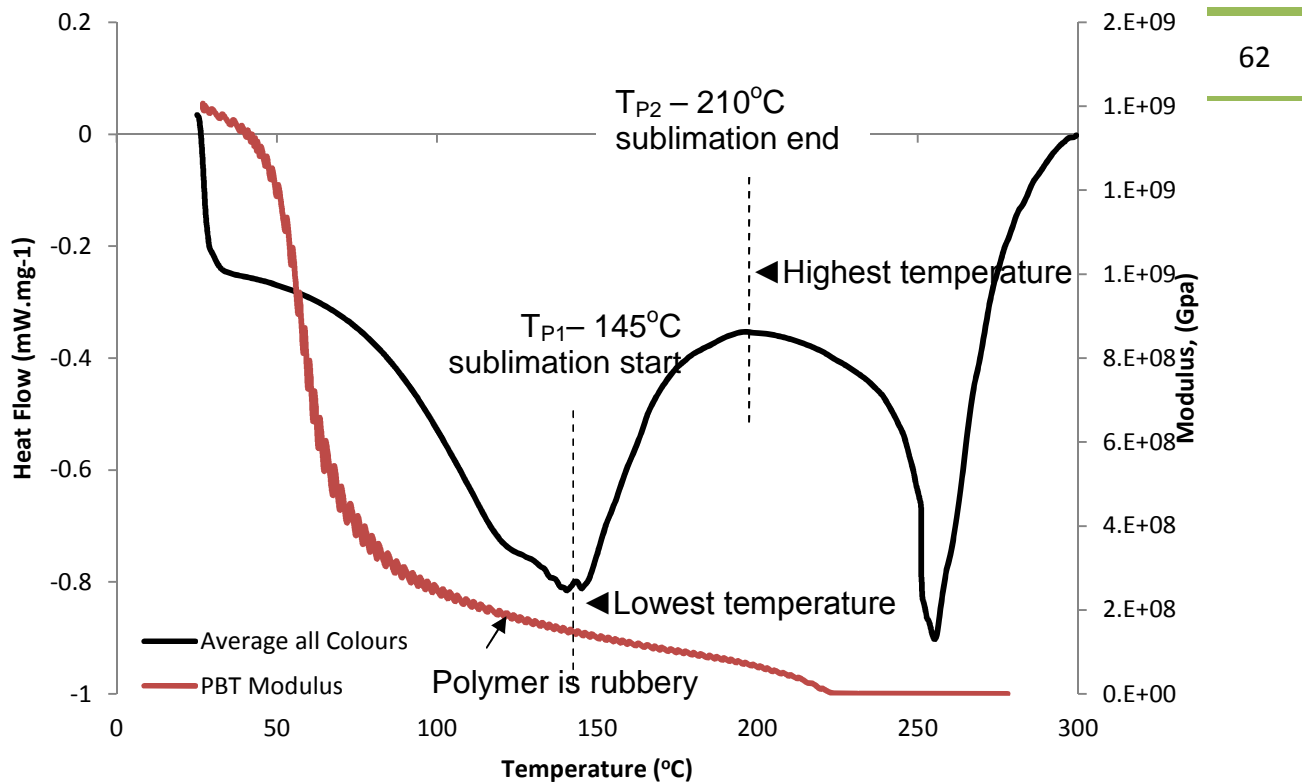
Figure 39 Average DSC results plotted with the DMTA results of PBT

Higher water content in the dyes result in lower thermal transition temperatures of T_{P1} and T_{P2}, for the "C" and "Y" colours. The DEG used in the dye material formulation could potentially chemically break down the surface of PBT substrates when processed at high temperatures and when large quantities of "M" and "K" colours are used.

The ramp rate experimentation revealed that as the heating rate increases so does the reaction kinetics, this is a typical result when heating rates are increased. However as the ramp rate is increased, T_{P3} remains stable and is believed to be a physical change to the DEG. Excessive temperatures for long processing times should be avoided to prevent the DEG from chemically attacking the polymer surface. Although this was not visibly observed by the author it is possible this could visibly affect the surface structure of the PBT especially when the decoration image has high levels of the "M" and "K" colours.

7. VISUALISATION OF THE DYE PENETRATION USING MATLAB

This section discusses and displays the results from the MATLAB program written to visualise the dye penetration depth into the PC or PBT substrates.

7.1. INTRODUCTION TO THE MATLAB PROGRAMME

The MATLAB program detailed in **portfolio submission 5**, was developed with the kind assistance of Dr M. McDonnell, Project Engineer MathWorks (McDonnell, 2010).

The purpose of the visualisation tool is to graphically represent the dye penetration depth in a material substrate. This is based on the data generated from the experimentation completed in section 3.2.2. Additionally it is intended that the tool can provide the user with data of the ideal time, temperature and level of dye penetration.

The dye sublimation process relies on a considerable amount of testing and evaluation time, 2-5 days to generate a consumer ready component (Barrow, 2010). A software based modelling tool would significantly reduce the costly sampling and measuring time, however one does not currently exist. Therefore the author selected Matlab to fulfil the needs of a dye penetration visualisation tool.

7.2. THE MATLAB PROGRAMME

The program consists of 4 subroutines, which are titled "Example", "Import Data", "Interpolate Data" and "Plot Data" these are described briefly below and the actual code can be found in **portfolio submission 5**.

The "Example" subroutine is the user interface which enables the import, interpolate data and plot data subroutines to function. During execution of the program, the "Example" subroutine enables the user to select the data file, which is handled in a Microsoft Excel spreadsheet. The "Import Data" subroutine allows the raw data to be imported from a Microsoft Excel spreadsheet, providing the data is formatted with times in rows and temperatures in columns.

The "Interpolate" subroutine allows for the generation of 20 new data points, between the imported data, this provides a 1 ^{o}C resolution of data.

The final subroutine, "Plot Data" takes the interpolated data and generates two graphical plots of the data. The first plot is a three dimensional surface plot with time on the x-axis, temperature on the y-axis and dye penetration depth on the z-axis, an example can be seen in Figure 40. The plot shows the data cursor, where "x" is time at 80 seconds, "y" is temperature at 160 ^{o}C and the dye penetration depth is 22.5 µm.
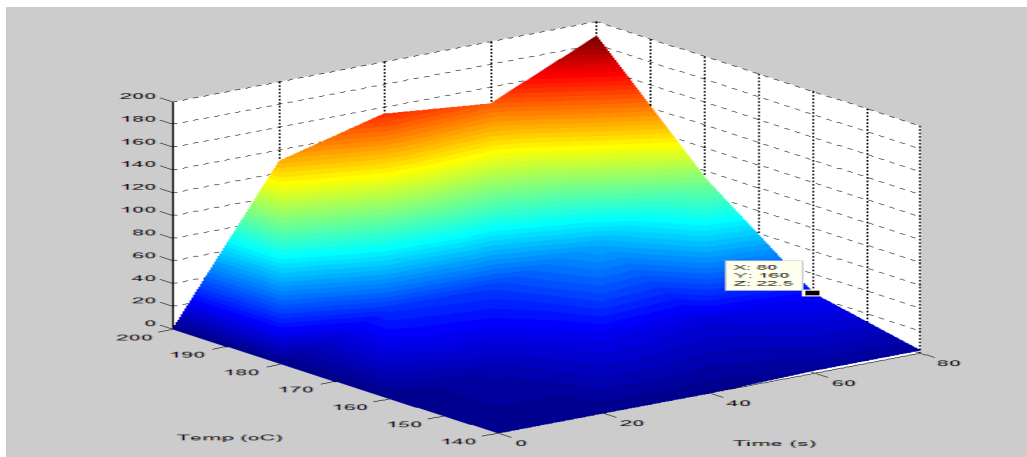
Figure 40 PBT "C" surface graph of the dye penetration depth

The second plot is a contour graph as illustrated in Figure 41, this shows time on the x-axis, temperature on the y-axis and dye penetration depth as a series of coloured contours.
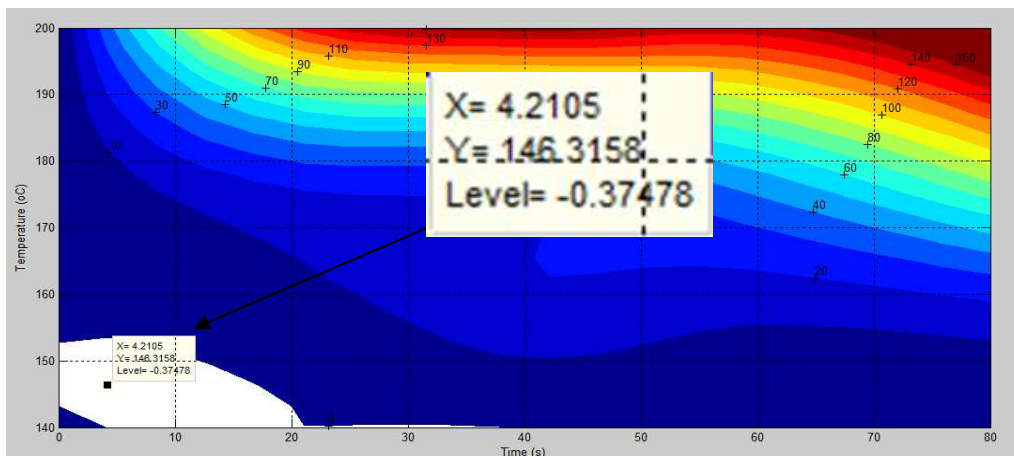
Figure 41 PBT "C" contour plot data of the dye penetration depth

The data cursor can be used to manually interrogate the plot to acquire time, temperature vectors and dye penetration depth. Figure 41 illustrates an example plot, the coloured bands visualise the dye penetration boundaries in 10 µm steps. The data cursor shows the temperature and time set to 146.32 $^{\circ}$C, 4.21 seconds resulting in a dye penetration depth of 0.37478 µm.

7.3. GRAPHICAL OUTPUTS

The following sections show the Matlab output graphs of the PC and PBT sections 7.3.1 and 7.3.2 respectively.

7.3.1. PC GRAPHICAL OUTPUTS OF THE DYE PENETRATION DEPTH

The plots in Figure 42 show the contour plots for the PC polymer in the individual CMYK colours.
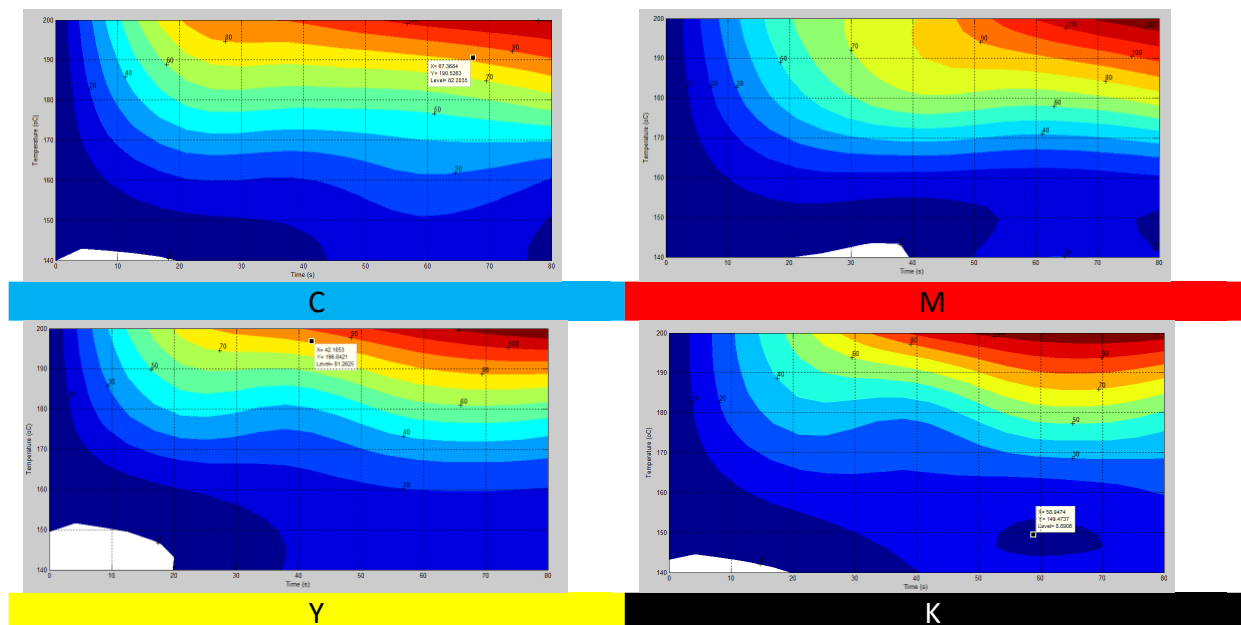
Figure 42 PC Individual contour plots of CMYK colours

Figure 43 shows the contour plot for the average PC data values, this is the most relevant to the user, in most instances the CMYK colours would be printed together to create the graphical image for the consumer, **portfolio submission 3**, section 5.

The contour plot shows a uniform dye penetration depth from 20-110 µm. If a dye penetration depth of 10 µm is required (shown as the deep blue colour) the process must be operated using a temperature of 140-150 ^{o}C and up to 45 seconds time or alternatively at the full temperature range at a time of <4 seconds. The plot shows that between 45-80 seconds using 140-160 ^{o}C a 20 µm dye penetration depth is achievable. The plot shows that in the white area no dye penetration is possible, 140-145 ^{o}C, ≤ 20 seconds. This guides the user into not decorating at these settings to avoid making parts with no dye penetration resulting in poor aesthetic quality.
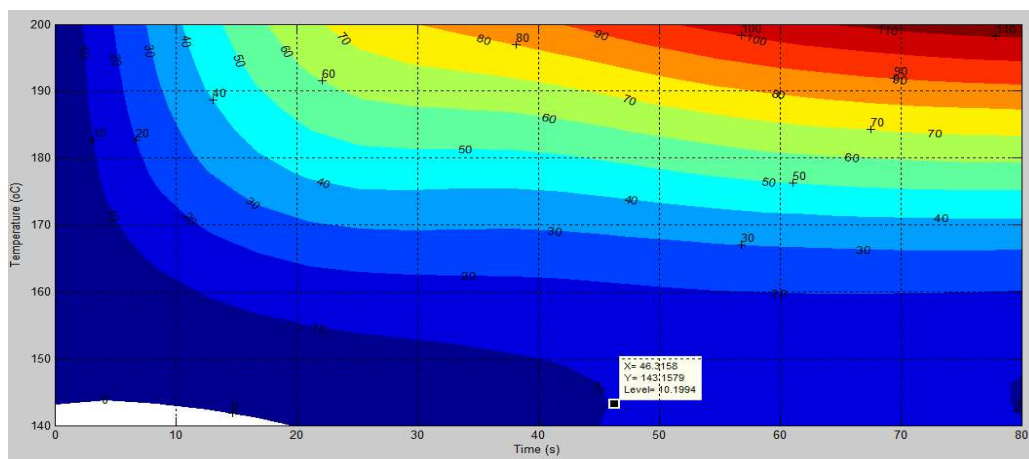
Figure 43 PC Contour plot of average dye penetration depth

7.3.2. PBT GRAPHICAL OUTPUTS OF THE DYE PENETRATION DEPTH

The plots in Figure 44 are for the PBT polymer using the individual CMYK colours..
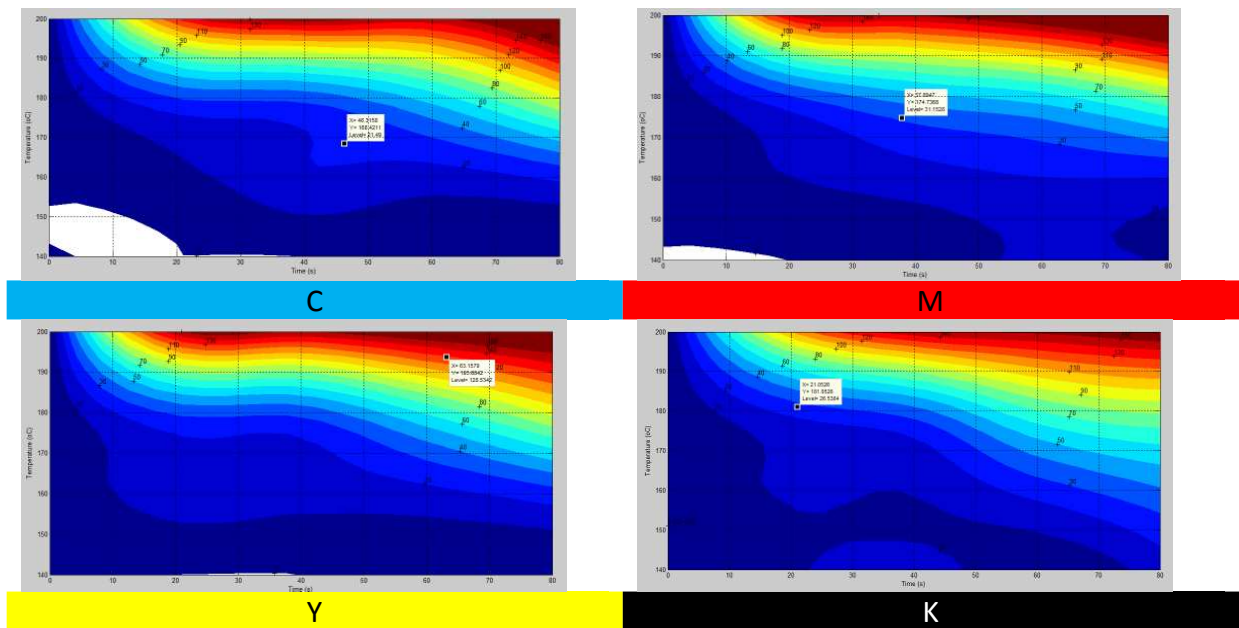
Figure 44 PBT Individual contour plots of CMYK colours

The plot shown in Figure 45 displays a uniform level of dye penetration at 10–150 μm. To achieve a 10 μm dye penetration depth, the processing parameters of 140–150 ^{o}C, 0–80 seconds or 150–160 ^{o}C, 0–20 seconds or 160–180 ^{o}C, 0–10 seconds, need to be selected. Unlike the contour plot shown for PC in Figure 43, there are no areas that show zero penetration of the dyes.
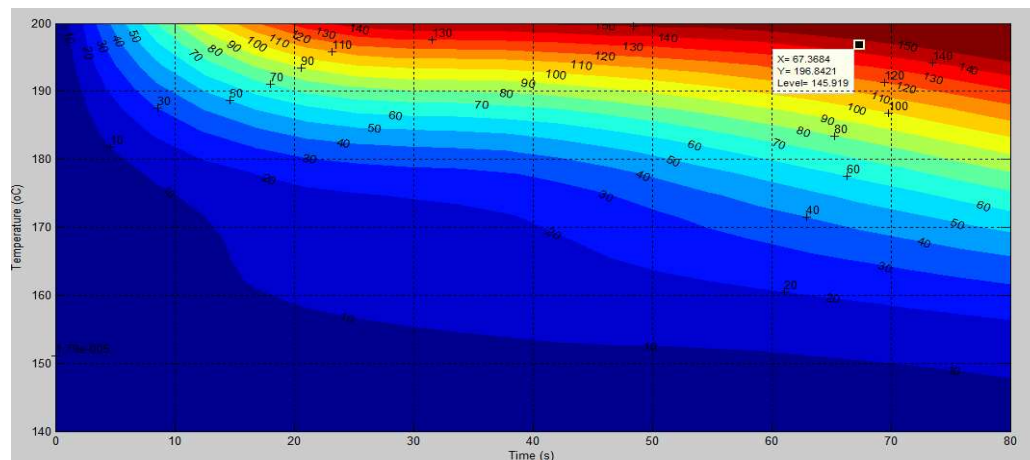
Figure 45 PBT Contour plot of average dye penetration depth

7.4. SECTION CONCLUSIONS

No tools are available to visualise dye penetration data from the dye sublimation process. The newly created visualisation tool performs well by taking in the existing data, interpolating it and outputting the data graphically. It guides the user to select settings in the process to achieve a desired level of dye penetration in the final part. The results enable the user to speed up the setting up time and reduce the number of parts typically destroyed. The tool works well and is currently under review at IDT, limitations have been identified and are listed in section 10.

8. OVERALL CONCLUSIONS TO THE RESEARCH

This section concludes on all of the research undertaken for the authors' Engineering Doctorate, it is arranged to address the knowledge gaps raised in section 2.1. Addressing these knowledge gaps demonstrates innovations as desired by the Engineering Doctorate.

> *(1) Data presented by Adams (Adams, 2007) illustrated in Figure 3, show that the dyes sublimate into semi-crystalline polymers more than the amorphous polymers, no reason is given for this condition.*

The experimental work detailed in sections 3 and 4 challenges previously published work. It recognises that amorphous polymers, previously thought to be unsuitable, can be used successfully in the dye sublimation process. This opens up the possibilities for material selection for those considering this technique for the decoration of their products.

Initial experiments confirmed that various levels of dye penetration can be achieved when semi-crystalline and amorphous polymers are used. Extensive experimentation on PC and PBT identified that the time and temperature have a significant effect on the level of dye penetration into the polymer; the highest level of dye penetration for PC was 116 µm and for PBT 179 µm. Process settings to achieve acceptably decorated components are identified in Table 15.

Further research acknowledged that the free volume of the polymer materials enables penetration and transportation of the dyes. It can be assumed from the research the amorphous PC polymer has a free volume of 2.5% below T_g and 11.3% above. The semi-crystalline PBT has a respective free volume of 1.5–1.6% below T_g and 6.78–7.34% above. This research has also identified that the visual condition of the surface with respect to the decoration and thermal damage must also be considered to ensure an acceptable component can be produced. Finally, the experimentation has provided a robust methodology for specimen preparation and evaluation for dye penetration depth.

(2) The data presented by Adams (Adams, 2007) does not inform the author how the CMYK colours perform in the different polymers. This is another area of investigation by the author.

The results highlighted that there are differences in the level of CMYK dye penetration into different polymers types. Tables 9 and 10 contain the visual results of the dyes penetrating the deepest or shallowest levels. Whist there are some patterns in the depth performance of the CMYK colours these do not vary by a large amount.

For the PBT polymer the average results show that there is only 4 μm difference between the "M" and "K" dyes. This is not envisaged to be a significant value as it only equates to 5–16% of the "target" dye penetration depth.

The average dye penetration results for the PC shows a range of 6 μm between the colours this could be deemed as significant if a constant dye penetration depth is required. The "C" gives the highest average value and the "K" gives the lowest.

The low range of dye penetration results between the CMYK colours is highly desirable to the surface decoration community. Quite often the colour pallet is generated by using a combination of the CMYK dyes and the results show no significant increase or decrease in dye penetration.

(3) No published information is available of the thermal characteristics of the sublimation dyes and how these relate to the substrate polymers. Experimentation to characterise the sublimation dyes will provide this knowledge.

The experimentation described in sections 3.3.3 and 5 of this innovation report have been completed to individually characterise the CMYK sublimation dyes, using DSC. The key thermal transitions of the individual colours were identified and the start and end of sublimation was confirmed visually. T_{P1} was confirmed as being the start of sublimation with a range of 119–145 ^{o}C and T_{P2} was identified as being the end of sublimation with a range of 173-210 ^{o}C. The graph in Figure 37 illustrates an excellent correlation of the dyes sublimating and the dye penetrating into the PC and PBT substrates.

The DSC results imply that amorphous polymers should have a $T_g \geq T_{P1}$ of the dye materials. This would ensure that the substrate polymers are able to withstand the high processing temperature and the dye materials have commenced sublimation. The temperature at which the polymer is fully liquid needs to be high enough to enable the dye materials to sublimate into the maximum possible free volume that can be achieved. For semi-crystalline materials the polymer needs to have a $T_g \leq T_{P1}$ to ensure that the free volume has increased prior to the start of the dye material sublimating. Ideally the polymer should have a $T_m \geq T_{P2}$ of the dye materials, ensuring that it is in a rubbery condition, enabling the sublimated dyes to penetrate the enlarged free volume.

Higher water content in the dyes result in lower temperatures for T_{P1} and T_{P2}, for the "C" and "Y" colours. The DEG used in the dye material formulation could potentially chemically break down the surface of PBT substrates when processed at high temperatures and when large quantities of "M" and "K" colours are used.

(4) There are no commercially available tools for the visualisation of dye penetration depth. Such a tool could be used to speed up product development time and reduce the number of parts physically destroyed.

This knowledge gap was addressed by the development of the dye penetration visualisation tool using MATLAB. The programming code was completed in MATLAB by importing formatted data, interpolating the results and generating output plots. The output plots enable the user to visualise the dye penetration depth and select time and temperature vectors. The results of the average dye penetration for the CMYK dyes are principally used to enable faster setting up times and reduce the number of parts physically destroyed during the setting up process. The tool works well and is currently under review at IDT, where the cost of the software versus the actual benefits is being assessed.

9. BENEFITS OF THE RESEARCH TO IDT SYSTEMS LIMITED

The following sections identify the innovations from the research which are of benefit to IDT.

9.1. BENEFITS FROM THE DYE PENETRATION EXPERIMENTATION

- The knowledge to select a polymer for the process which has a high enough T_g to enable daily use of the product.

- The additional use of amorphous PC is now possible with a high level of dye penetration achieved into the polymer.

- The identification of both polymer surface condition and dye penetration depth as important considerations of the process.

- The methodology used in this research can be used with other polymer types to establish process suitability.

- Investigation of the commercial use of the "extended" free volume technique.

- Re-evaluation of acceptable limits for dye penetration depths, 15-75 μm.

- Processing window recommendations for time and temperature are shown in Table 15.

9.2. BENEFITS FROM THE THERMAL CHARACTERISATION OF THE DYE MATERIALS

- For a simple quality control procedure, the potential to investigate the possibility of measuring the water content of the dye materials. Too much or too little water content of the dye material may affect the temperature of T_{P1} and T_{P2} leading to incorrect processing and poor dye penetration into the polymer. This would be a more cost effective solution for IDT than purchasing a DSC for the proposal described below.

- Investigate using the DSC technique as a quality control measure of the dye materials, to ensure the sublimation characteristics remain acceptable.

- Use the "ideal" temperatures for T_{P1} and T_{P2} to characterise the selection criteria of the amorphous and semi-crystalline substrate materials.

- The potential to investigate other sublimation dye materials to identify suppliers who use less DEG in the composition, so that the process can be operated at higher temperatures without possible issues of the dye materials effecting polyester material types.

9.3. BENEFITS OF THE MATLAB VISUALISATION TOOL

- The ability to use time and temperature settings to give a dye penetration depth in a predictive manner.
- Selecting a dye penetration depth and the required optimum parameters.
- Avoiding process settings whereby no dye is transferred into the product.
- Reducing the development time required to produce "acceptable" parts.
- Eliminating the need to carry out destructive testing on the components.
- Reducing component wastage and environmental disposal issues.

9.4. IMPACT TO PRODUCTION COSTS ADOPTING THE OPTIMISED PROCESS

The cost to operate a cycle of the transfer press, Table 16 has been calculated based on the assumptions provided by IDT (Jenner, 2011) and the recommended process conditions described in section 5.2.9.

Assumptions made:-

- Start and cooling temperature-25 and 45 ^{o}C respectively.
- Unloading and reloading time-1 minute.
- Ramp rate for heating and cooling-36 ^{o}C/min.
- Transfer press running cost-£120/hr.
- These costs do not include overheads, substrates, TC or dyes.

Table 16 Calculated process costs

Time	Temp	Time to temp	Time to cooling	Total process time	Total cycle time	Cycles per hour	Cost per cycle
(secs)	°C	(min:secs)					£
20	140	03:12	02:38	06:10	07:10	8.37	£14.34
	160	03:45	03:12	07:16	08:17	7.25	£16.56
	180	04:18	03:45	08:23	09:24	6.39	£18.78
	200	04:52	04:18	09:30	10:30	5.71	£21.01
40	140	03:12	02:38	06:30	07:30	8.00	£15.00
	160	03:45	03:12	07:36	08:37	6.97	£17.22
	180	04:18	03:45	08:43	09:43	6.17	£19.44
	200	04:52	04:18	09:50	10:50	5.54	£21.67
60	140	03:12	02:38	06:50	07:50	7.65	£15.68
	160	03:45	03:12	07:57	08:57	6.70	£17.90
	180	04:18	03:45	09:03	10:04	5.96	£20.13
	200	04:52	04:18	10:10	11:10	5.37	£22.35
80	140	03:12	02:38	07:10	08:10	7.34	£16.34
	160	03:45	03:12	08:16	09:17	6.46	£18.56
	180	04:18	03:45	09:23	10:24	5.77	£20.79
	200	04:52	04:18	10:30	11:30	5.22	£23.01

Table 17 displays the cost per cycle where satisfactory parts can be produced using PC and PBT substrates. The results show that the lowest cost to operate a cycle using PC substrates is £18.56 and the highest is £19.44 representing a difference of £0.88. The lowest cost to operate a cycle using PBT is £18.56 and the highest is £22.35 representing a £3.79 per cycle saving if processing at the lowest cost cycle.

Table 17 PC & PBT Cost per cycle to produce acceptable specimens

Polymer	Temperature (°C)	Time (seconds)			
		20	40	60	80
PC	140				
	160				£18.56
	180	£18.78	£19.44		
	200				
PBT	140				
	160				£18.56
	180	£18.78	£19.44	£20.13	£20.79
	200	£21.01	£21.67	£22.35	

The maximum possible cycles per annum is shown in Table 18 this calculation does not take into account, scrap or equipment downtime.

Assumptions made:-

- Number of hours per day-24.

- Days per week-5.

- Weeks per month-4.

- Months per annum-12.

Table 18 Number of acceptable cycles per annum using PC and PBT substrates

Polymer	Temperature (^{o}C)	Time (seconds)			
		20	40	60	80
PC	140				
	160				37,237
	180	36,796	35,547		
	200				
PBT	140				
	160				37,237
	180	36,796	35,547	34,345	33,253
	200	32,901	31,899	30,927	

Using PC 1,690 more cycles per annum can be operated if the process is set at 160 ^{o}C, 80 seconds when compared to 180 ^{o}C, 40 seconds. Using PBT processed at 160 ^{o}C, 80 seconds 6,310 additional cycles can be operated per annum compared to operating at 200 ^{o}C, 60 seconds.

This situation is further exaggerated if more than one substrate is decorated per cycle as the process is typically setup. For example decorating iPhone covers, IDT operates each cycle with 9 substrates in the process (Jenner, 2011). Using PC this equates to 15,210 and PBT 57,790 more decorated parts per annum.

10. LIMITATIONS OF THE RESEARCH AND FURTHER WORK

This section highlights the limitations of the research undertaken during this Engineering Doctorate and suggests further work to improve the understanding of the dye sublimation process.

The limitations and further work from the experimental work described in section 3.2.1 and 3.2.2 are listed below:-

- The experimentation used an initial time of 20 seconds. The value was provided from the industrial experience at IDT when trying to establish processing times the initial setting used 20 seconds (Barrow, 2010). However this does not provide data of what dye penetration can be expected when the process is set to <20 seconds.
  - It would be of benefit to the dye sublimation community if further studies were completed with the time range of 0-20 seconds. This will verify how much dye penetrates the polymer and the time at which it occurs.
- The experimental time was restricted to 80 seconds, from the research it is unclear at what point the time ceases to have any significant benefit to increasing the level of the dye penetration.
  - Further trials are required to determine at what point the time ceases to affect the level of dye penetration. This is of commercial benefit to industry as it could be determined where the processing time has no further benefit and what the resulting dye penetration depth is.
  - Investigate the thermal condition of the substrate polymers and what the thermal gradient is and at which point does the material become fully isothermal.
- It is unclear if there is dye movement within the polymer after the decoration process with time and possibly cause fading. Is there a different stability of image in the different polymer classes? Does this highlight a maximum temperature of exposure during life usage for components made with one polymer versus another?
  - Additional experimentation is required using the PC and PBT to verify if the decoration blurs fades or moves following the dye sublimation process and is this time and or temperature reelated.

- The materials PC (ELX 1414) and PBT (S600F20) are identified as being suitable candidate materials in this process. It is an assumption that this process would be suitable for similar PC and PBT polymers; however this is not confirmed.
    - o Complete the study on alternative grades of PC and PBT to determine the dye penetration depth performance and compare as discussed in this innovation report. This could be important if this could be determined with PBT's with different levels of crystallinity. Additionally the affect that pigments or fillers in the polymers can have on the level of dye penetration.

- This series of experiments identified that amorphous PC is suitable for the dye sublimation process however this does not confirm if other amorphous polymer types are suitable for this process and how much dye penetration could be expected.
    - o Using the methodology described in this report the alternative amorphous material types should be tested to confirm the potential of using these polymer types in the process and what the level of dye penetration could be. Table 9 shows other polymer types where differences between the dye sublimation depths between Adams (Adams, 2007) and the authors data generated in **portfolio submission 2** are highlighted. These would be ideal candidates for further experimentation.

- The theoretical or actual free volume of the polymers is unknown. This was due to the polymer supplier's reluctance to provide this information or insufficient knowledge of the polymer to complete the equations in section 5.2.5.
    - o Determine the free volume of the polymer by gaining information of the polymer, using analytical testing equipment. The properties to determine are the coefficient of thermal expansion above and below the Tg of the polymer and the Van der Waals Volume and to determine the actual level of crystallinity of the PBT.
    - o Investigate using the PALS technique, whereby electrons are injected into the polymer and their life time is measured, to determine the free volume of the polymer. Free volume in the polymer increase the lifetime of the electrons and therefore can be determined to be different compared the bulk of the polymer (Yampolskii et al., 2006).

- It is unknown how much of an effect the dyes, supplied by Sawgrass have on the level of dye penetration into the polymer.
  - Re-run the experiments using a different supplier of dyes to determine if the level of penetration is improved or worsened. This may highlight the penetrant size of the dyes whilst sublimated and their effectiveness of penetrating the free volume in the polymer.
- The method of measuring dye penetration depths was consistently completed by the author. However by using another researcher dissimilar dye penetration levels could be achieved.
  - Investigate alternative methods of establishing dye penetration, such as using software based or colour recognition systems to establish a more consistent approach to measurement.
- The dye penetration depth needs a higher level of controllability so that the actual depth is at a desired level, especially for other creative uses of the technology.
  - This work would be highly valuable if the dye sublimation of "conductive" dyes was carried out whereby these can be used to create three dimensional electronic linkages.

The limitations and further work from the thermal characterisation of the sublimation dyes described in section 6 are listed below:-

- The DSC testing of the dyes can be of benefit as additional knowledge of the thermal effects on the dyes can be acquired.
  - Complete DSC testing of the dye materials using iso-thermal temperature profiles to establish the effect on the dyes at T_{P1} and T_{P2}.
- The impact of the DEG to the surface of the PBT is a documented condition, based on existing scientific research and publications.
  - Conduct further experimentation to investigate the impact to the surface structure of the substrate material by using very small amounts of the DEG and the dye material at elevated temperatures.
- The DSC work was completed on the dyes supplied by SAWGRASS.
  - It would be worthwhile to complete further characterisation on competitive dyes to understand if they offer a better or worse process condition.

The limitations and further work from the MATLAB visualisation tool described in section 7 are listed below:-

- The visualisation tool does not allow for the errors in the dye penetration measurements that were discussed in section 5.2.6. Without knowing the upper and lower limits of the dye penetration depth the user may still need to complete some testing albeit at a "lower level" to ensure they have the desired level of dye penetration.

  o Further develop the MATLAB code to include the error measurements at a recommended +/- 1 standard deviation. The output to the user would provide the time and temperature vectors and the dye penetration depth with upper and lower measurements.

- The raw data generated is specific for the grades of PC and PBT used in the experimentation and testing.

  o Further experiments and testing would be required for other grades of PC and PBT to establish if these materials give similar or disparate levels of dye penetration. The ideal scenario would be to have a set of data that could be used in all instances of amorphous and semi-crystalline polymer types.

11. REFERENCES

- ADAMS, L. (2007). To Dye For, Process decorates plastics in three dimensions. Appliance Design, 55, 37-41.

- ADAMS, L. (2010). Editor Appiliance Design Magazine, (http://www.appliancedesign.com/), E-Mail Communication regarding the published article in Appliance Design, Information Requested Regarding the Penetration of Dyes into Polymer Substrates, Contact : adamsl@bnpmedia.com, E-Mail Communication, [Contacted 2010].

- ANON (2005). Decoration by sublimation of 3-D plastics parts goes commercial, Available from:http://plastics.dupont.com/myplastics/Mediator?common=5,4895,5267&locale=ko_KO, Accessed:[June 2010]. In: DUPONT (ed.). Dupont.

- ANON. (1997). Seiko Instruments' New ColorWear Transfer Media and Dye-Diffusion Fabric Transfer Process Creates an Industry Breakthrough for the Specialty Imprinting Market; Exclusive Media and Continuous Tone Dye Diffusion Process Offers Specialty Printers and Business Owners a Cost-Effective, Short-Print-Run Solution to Transfer Photo-Realistic Images and Color Graphics Onto Cotton and Cotton-Blend Fabrics. Business Wire [Online].

- ARNOLD, J. C. (2010). A free-volume hole-filling model for the solubility of liquid molecules in glassy polymers 2: Experimental validation. European Polymer Journal, 46, 1141-1150.

- BAMBERG, M. (2005). Digital Art Photography for Dummies, Hoboken, USA, John Wiley & Sons.

- BARROW, N. (2010). Polymer and Materials Specialist, IDT Systems Ltd, The Factory, Dippenhall, Farnham, Surrey, GU10 5DW, Various general discussions regarding the Dye Sublimation process and research needs, Contact : nigel.barrow@idt-systems.com, Verbal and E-Mail Communication, [Contacted 2010-2011].

- BERINS. M, L. (1991). Plastics Engineers Handbook of the Society of the Plastics Industry, UK, Chapman and Hall.

- BOHLEN, J. & KIRCHHEIM, R. (2001). Macroscopic Volume Changes versus Changes of Free Volume As Determined by Positron Annihilation Spectroscopy for Polycarbonate and Polystyrene. Macromolecules, 34, 4210-4215.

- BROWN, R. (1828) A brief description of microscopical observations made in the months of June, July and August 1827, on the particles contained in the pollen of plants; and on the general existence of active molecules in organic and inorganic bodies. Ann. Phys. 14, 294–313.

- BROWN, M. E. (2001). Introduction to thermal analysis: techniques and applications, Norwell, USA, Kluwer Academic Publishers.

- BRINKMAN, H. C. (1956) Brownian motion in a field of force and the diffusion theory of chemical reactions, Physica, 22, 29-34.

- BUDD, P. M. & MCKEOWN, N. B. (2010). Highly permeable polymers for gas separation membranes. Polymer Chemistry, 1, 63-68.

- BUDD, P. M., MCKEOWN, N. B. & FRITSCH, D. (2005a). Free volume and intrinsic microporosity in polymers. Journal of Materials Chemistry, 15, 1977-1986.

- BUDD, P. M., MSAYIB, K. J., TATTERSHALL, C. E., GHANEM, B. S., REYNOLDS, K. J., MCKEOWN, N. B. & FRITSCH, D. (2005b). Gas separation membranes from polymers of intrinsic microporosity. Journal of Membrane Science, 251, 263-269.

- BURKINSHAW, S. M. 1995. Chemical principles of synthetic fibre dyeing, Glasgow, UK, Blackie Academic & Professional.

- CHANDLER, S. (2007). Creating Indelible Images, Ceramic Industry, Available from : <http://www.ceramicindustry.com/Articles/Feature_Article/BNP_GUID_9-5-2006_A_10000000000000077685>, [Accessed June 2010].

- CHAVAN, R. B. & JAIN, A. K. (1988). The role of ethylene glycols during sublimation transfer printing of cotton. Journal of the Society of Dyers and Colourists, 104, 220-223.

- CHERVIN, C. (2010). European Extrusion Technology Leader, DuPont de Nemours, (http://www2.dupont.com/DuPont_Home/en_US/index.html), E-Mail Communication regarding the published article in Appliance Design, Information Requested Regarding the Penetration of Dyes into Polymer Substrates, Contact : Christophe.Chervin@CHE.dupont.com, E-Mail Communication, [Contacted 2010].

- CHERYAN, M. (1998) Ultrafiltration And Microfiltration Handbook, Bota Rotan, Florida, CRC Press

- COATES, R. (2010). Automotive Development, DuPont Performance Polymers, DuPont U.K. Limited, Wedgwood Way, Stevenage, Herts, SG1 4QN, Communication regarding the crystallinity of PBT polymers, Contact : Robert.J.Coates@gbr.dupont.com, Verbal and E-mail Communication, [Contacted 2010].

- COBB, J. (2010). Director of Product Development. Sawgrass Technologies, 2233 US Hwy 17 North, Mount Pleasant, website : www.sawgrassink.com, Contact : jcobb@sawgrassink.com, Verbal and E-mail Communication [Contacted Jan 2010]. Type to MAKENJI, M. K.

- CONSOLATI, G. (2007). Temperature dependence of nanoholes free volumes in amorphous polymers. Radiation Physics and Chemistry, 76, 313-317.

- CRANK, J. PARK, G. S. (1968) Diffusion in Polymers, London, UK, Academic Press

- DLUBEK, G., SAARINEN, K. & FRETWELL, H. M. (1998). The temperature dependence of the local free volume in polyethylene and polytetrafluoroethylene: A positron lifetime study. Journal of Polymer Science Part B: Polymer Physics, 36, 1513-1528.

- FAKIROV, S. (2005). Handbook of Thermoplastic Polyesters, Berlin, Germany, Wiley-VCH Verlag GmbH & Co. KGaA.

- FLICK, E. W. (1998). Industrial solvents handbook, New Jersey, USA, Noyes Data Corp.

- FICK, A. (1855) Poggendorff's Annalen. 94, 59-86. and (in English) Phil.Mag. 10, 30-39.

- GRAUSE, G., KAMINSKY, W. & FAHRBACH, G. (2004). Hydrolysis of poly(ethylene terephthalate) in a fluidised bed reactor. Polymer Degradation and Stability, 85, 571 - 575.

- GREGORY, P. (1991). High-technology applications of organic colorants, New York, USA, Plenum Press.

- HATAKEYAMA, T. & QUINN, F. X. (1999). Thermal analysis : fundamentals and applications to polymer science, Chichester, Chichester, UK, John Wiley.

- HÖHNE, G., HEMMINGER, W. & FLAMMERSHEIM, H. J. (2003). Differential scanning calorimetry, Verlag, Berlin, Heidelberg, New York, Springer.

- ITS-MY-CASE (2011). Available from:[https://www.itsmycase.com/Home.aspx], Accessed: [2011].

- JENNER, A. (2011). Business Manager, IDT Systems Ltd, The Factory, Dippenhall, Farnham, Surrey, GU10 5DW, Various general discussions regarding the cost of operating the Dye Sublimation process and research needs, Contact : adrian.jenner@idt-systems.com, Verbal and E-Mail Communication, [Contacted Sept 2011].

- KEATING, M. Y. (1998). High glass transitions of high-performance thermoplastics. Thermochimica Acta, 319, 201-212.

- LEE, H. C. (2005). Introduction to color imaging science, Cambridge, UK, Cambridge University Press.

- LEFFINGWELL, G., LESSER, M. A. & BENNETT, H. (1945). Glycerin, its industrial and commercial applications, New York, USA, Chemical publishing co., inc.

- LOVE, J. C. & GOODSHIP, V. (2002). In-Mould Decoration of Plastics, Shrewsbury, UK, Rapra Technology Ltd.

- LUTZOW, N., TIHMINLIOGLUA, A., DANNERA, R., WARNIER, G. & ZIELINSKI, J. (1999). Diffusion of toluene and n-heptane in polyethylenes of different crystallinity. Polymer, 40, 2797-2803.

- MAKENJI, K. & BAUMBER, K. (2010). Improvements in Dye Sublimation, GB2470195. GB published patent.

- MAKENJI, K. (2010). Entry for University of Warwick Poster Competition - The implications for the decoration of plastic parts. In: University of Warwick.

- MAKENJI, K. (2011). Dye Sublimation — Variation of Dye Penetration Depths with Semi-Crystalline and Amorphous Polymers. Progress in Rubber and Plastics Technology, 11, 69-84.

- MAKENJI, K. PEARCE, B. (2009). Surface Decoration as a Means of Cost Saving: Developments at WMG, Managing the Cost of Technology. Foresight Vehicle Conference. WMG, University of Warwick.

- MARGOLIS, J. M. & MEYER, F. J. (1986). Decorating plastics, Munich, Germany, Hanser Publishers.

- MARK, H. F. (2007). Encyclopedia of polymer science and technology, Hoboken, N.J., Wiley-Interscience.

- MCDONNELL, M. (2010). Project Engineer, Mathworks, Matrix House, Cambridge Business Park, Cambridge, CB4 0HH, Support and training for the development of the Matlab code, Contact : matt.mcdonnell@mathworks.co.uk, Verbal and E-Mail Communication, [Contacted 2010].

- MEYER, R. (1975). Aqueous ink for use in the Ink Jet Process, Patent Number 3, 889, 269.

- ORTOLANI, J. (2006). Don't Wait - Sublimate! Stitches Magazine Overland Park 20.

- PAGLIARO, M. & ROSSI, M. (2010). Future of Glycerol, RSC Green Series Number 8, Cambridge, UK, Royal Society of Chemistry.

- PARDAL, F. & TERSAC, G. (2006). Comparative reactivity of glycols in PET glycolysis. Polymer Degradation and Stability, 91, 2567 - 2578.

- RAJESH, S. & RAMESH, C. (2002). Recycling of polybutylene terephthalate waste: oligomer preparation and subsequent solid state polymerization into high molecular weight polymer. Macro-2002: Seventh National Conference of the Society for Polymer Science, India, The International Seminar on Frontiers of Polymer Science and Engineering, Kharagpur, India. Kharagpur, India.

- REZAC, M. E. & JOHN, T. (1998). Correlation of penetrant transport with polymer free volume: Additional evidence from block copolymers. Polymer, 39, 599-603.

- RODGERS, P. A. (1993). Pressure–volume–temperature relationships for polymeric liquids: A review of equations of state and their characteristic parameters for 56 polymers. Journal of Applied Polymer Science, 48, 1061-1080.

- SAWGRASS (2008). SubliJet IQ, Material Safety Data Sheet, CMYK, Available from :< http://www.sawgrassink.com/technical-support/sublijet/msds>, [Accessed June 2010].

- SCHEIRS, J. & KAMINSKY, W. (2006). Feedstock recycling and pyrolysis of waste plastics : converting waste plastics into diesel and other fuels, Chichester, UK ; Hoboken, NJ, J. Wiley & Sons.

- SEITZ, J. T. (1993). The estimation of mechanical properties of polymers from molecular structure. Journal of Applied Polymer Science, 49, 1331-1351.

- SHEARMUR, T. E., DREW, D. W., CLOUGH, A. S., VAN DER GRINTEN, M. G. D. & SLARK, A. T. (1996). Study of dye diffusion in polymers using Rutherford backscattering. Polymer, 37, 2695-2700.

- SHERMAN, L. (2005). Dye Sublimation Printing: Durable Color Decoration for 3D Parts : Plastics Technology, Available from: <http://www.ptonline.com/articles/dye-sublimation-printing-durable-color-decoration-for-3d-parts>. 2005. Available: http://www.ptonline.com/articles/dye-sublimation-printing-durable-color-decoration-for-3d-parts [Accessed Jan 2010].

- SIMHA, R. & BOYER, R. F. (1962). On a General Relation Involving the Glass Temperature and Coefficients of Expansion of Polymers. The Journal of Chemical Physics, 37, 1003-1007.

- SIMHA, R. & CARRI, G. (1994). Free volume, hole theory and thermal properties. Journal of Polymer Science Part B: Polymer Physics, 32, 2645-2651.

- SIMHA, R. (1977). Configurational Thermodynamics of the Liquid and Glassy Polymeric States. Macromolecules, 10, 1025-1030.

- SLARK, A. T. & HADGETT, P. M. (1999). The effect of specific interactions on dye transport in polymers above the glass transition. Polymer, 40, 4001-4011.

- SMITH, G. F. & EASTERLOW, R. (1996). New method for manufacturing painted components. Plastics and Rubber Composites and Applications, 25, 116.

- STOREY, J. (1975). Textile Printing, London, UK, The Thames and Hudson Manuals.
- STOYE, D. & FREITAG, W. (2007). Introduction, in Paints, Coatings and Solvents, Berlin, Germany, Wiley-VCH Verlag GmbH.
- VEITH, R. (1991). Diffusion In and Through Polymers, Principles and Applications, Munich, Germany, , Carl Hanser Verlag.
- WARD, I. M. & SWEENEY, J. (2004). An introduction to the mechanical properties of solid polymers, West Sussex, England, Wiley.
- WHITE, J. (2010). The Story Of Stuff, Available from:<http://www.greenprophet.com/2010/08/mazzy-story-of-stuff/., Accessed: [2010].
- WHO'S-ON-YOUR-CASE (2011). Avaialble from:[http://www.whosonyourcase.com], Accessed: [2011].
- WILLIAMS, P. (2011). Product Specialist - Thermal Analysis, Mettler Toledo Ltd, 64 Boston Road, Beaumont Leys, Leicester LE4 1AW, Mobile Tel: 07884 238330, Office Tel: 0116 235 7070, Personal communication regarding the thermal chracterisation of sublimation dyes Contact : Phil.Williams@mt.com, Email and Verbal Communication [2011].
- WILLMORE, F. T., WANG, X. & SANCHEZ, I. C. (2006). Free volume properties of model fluids and polymers: Shape and connectivity. Journal of Polymer Science Part B: Polymer Physics, 44, 1385-1393.
- WOODD, P. (2011). CEO, IDT Systems Ltd, The Factory, Dippenhall, Farnham, Surrey, GU10 5DW, Statement regarding the impact of the Engineering Doctorate research, Contact : peter.woodd@idt-systems.com, Verbal and E-Mail Communication, [Contacted Oct 2011].
- YAMPOLSKII, Y., PINNAU, I. & FREEMAN, B. D. (2006). Materials science of membranes for gas and vapor separation, Chichester, UK, Wiley.
- YOON, C. & CHOI, J.-H. (2008). Syntheses of polymeric dispersants for pigmented ink-jet inks. Coloration Technology, 124, 355-363.
- XANTHOS, M. & TODD, D. B. (2002). Plastics Processing. Encyclopedia of Polymer Science and Technology. New Jersey, USA, John Wiley & Sons, Inc.