Dye Sublimation - Variation of Dye Penetration Depths with Semi-Crystalline and Amorphous Polymers

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SUMMARY

The dye sublimation process is used to decorate the surfaces of plastic, coated metal and ceramic components. Limited data is published on the performance of polymers under this process, and these findings show there are differences in the performance of amorphous and semi-crystalline polymers. The reason for these differences was investigated. Experimentation was conducted on a range of semi-crystalline and amorphous polymers. These were decorated using a standard cyan, magenta, yellow and black pattern. The level of dye penetration was measured using optical microscopy. It was found that the dye penetrated the semi-crystalline polymers approximately ten times more than in the amorphous polymers. There are disparities between the measured values here and previously published data. These disparities were found to exist as a result of large operating processing temperatures and times.

1. INTRODUCTION

Dye diffusion (also known as thermal transfer) is the process of using specialist inks to print an image onto a carrier and transfer it into a substrate. It was first known as the Star Transfer method and was developed by an Italian textile print company called Stampa Tessuti Artistica of Milan, during the early 1950's. ICI took out patents in 1952 which later lapsed due to initial lack of technology take up, it later became popular in the 1960's [1].

The dyes used in the process sublimate at elevated temperatures. The process of sublimation is where the inks transform from the solid phase to the gaseous phase without the intermediate formation of a liquid phase [2].

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The sublimation process is used extensively in the textile industry as a means to mass customise garments with individual designs. The process lends itself to this market well, as the printing is a digital process which enables designs to be different from each other. With improvements in ink and printer technologies this process has been used extensively in other markets where mass customisation is desirable. For example, power outlets and electrical sockets can be customised to individual designs [3]; the process enables a high level of mass customisation without incurring additional costs. The process is also used in security applications; access and identification cards are printed using this technology and the mass customisation aspect of the process is a definite strength as each card needs to be differentiated from the previous one [4]. Other industries where dye sublimation is used are the decoration of archery bows, gun stocks and all terrain vehicles [1].

The latest iteration of the process enables the processor to print into three dimensional components using vacuum forming technology. These systems are commercially available by IDT-Systems Ltd, ICI ImageData, Kolorfusion and E-Chameleon. All of these systems are based on a similar technology of a three dimension printing technique [5, 6, 7].

For the purpose of describing the technique the author will outline the i-SDS process developed and marketed by IDT-Systems Ltd (Dippenhall, UK), shown in **Figure 1**. The images show the graphical capabilities of their system and the ability to cope with complex geometries.

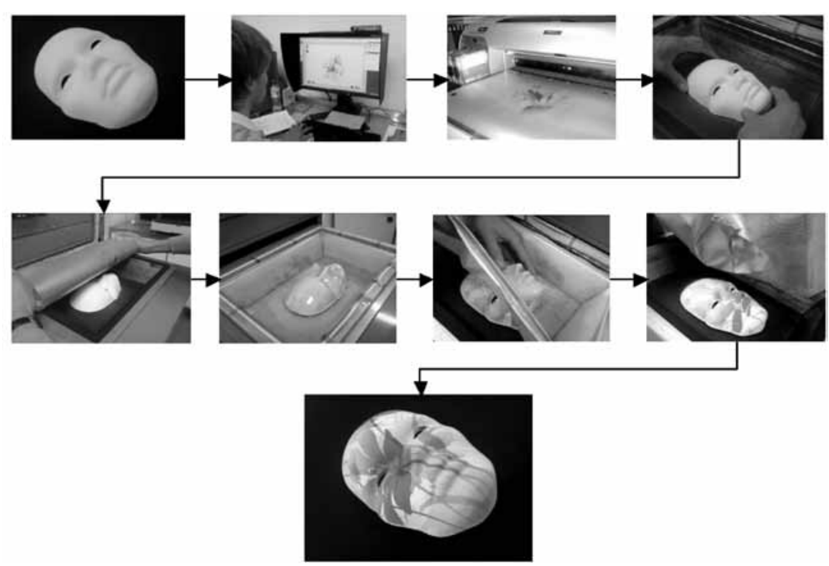

***Figure 1**. The IDT Systems Ltd transfer process (images courtesy of IDT Systems Limited, Dec 2009)*

The first image shows the blank substrate in the form of a plastic facemask. A digital image is then printed onto a special transfer carrier using the special dye sublimation inks. The plastic facemask is loaded into the transfer press which applies process heat and vacuum.

During this stage in the process the transfer carrier is thermoformed around the substrate and the inks are sublimated at an elevated temperature, these are then transferred into the polymer substrate. The transfer carrier is removed with the image visibly transferred into the surface of the mask.

The printers used in the process are inkjet based and can be of a standard unmodified equipment type. The print head lays down one droplet of ink at a time on to the carrier medium until the image is fully generated. The ink colours are delivered individually as Cyan, Magenta, Yellow and Black, (CMYK); there can be up to 16.7 million colours when these colours are used in combinations. Dye sublimation enables a printed image to be a higher resolution than the original print. As an example if an image is printed at 300 dots per inch, (dpi), then the resulting dye sublimated image can be at a resolution in excess of 2400 dpi [8].

In the standard dye sublimation process, a transfer press is used to heat up the dyes to transfer them to the desired substrate. The transfer press is a simple device to enable heat to be transferred from the printed carrier film to the part. Also the press enables contact between a heater element situated in the platen, the film and the substrate. The temperatures required by the transfer press must be sufficient to allow the inks to sublime. Some of the transfer presses are of a clam shell design; there is a fixed and floating platen. Some machine designs allow the top platen to swing out of the way for process preparation. The design of machine must have a sufficient gap to allow the printed film and substrate to fit in. The process of sublimation in the heated press can take from 6 – 8 minutes.

A transfer press with a vacuum pump is used when three dimensional components are used in the dye diffusion process. The vacuum is applied to the underside of the print carrier, when the carrier has softened with heat. The applied vacuum enables the print carrier to conform to the substrate [9].

2. MATERIALS USED IN THE DYE SUBLIMATION PROCESS

The key materials used in the dye sublimation are the transfer carrier, the inks and the substrate.

The transfer carrier traditionally used for flat geometry components is a paper based product. It has no coatings applied to the surface; however it has a specific structure to prevent the penetration of the sublimation inks during printing. In the case of three dimensional parts a polymeric film is used with a release coating. The film is vacuum formed to the substrate component enabling it to comply with the geometry [9, 10].

Polymers can be easily decorated and literature suggests that semi-crystalline polymer perform better than amorphous types. Glass, wood, metal and ceramics can also be decorated in the process but must be coated with a receptive layer prior to dye sublimation. The dyes are then sublimated into the receptive layer. Anodised aluminium can also be used in the process, but the sublimation must take place prior to sealing the anodic coating [11].

Depth of penetration of the dye into polymers is dependent on the glass transition temperature of the polymer. The process varies but the temperature of the dye transfer is typically 250°C for a duration of 12 ms. Kolorfusion state that the minimum temperature the polymer can withstand should be 138°C [12, 13]. **Figure 2** shows different levels of dye penetration in both semi-crystalline and amorphous polymers.

The inks used in the process are water based and contain disperse dyes based on antraquinonic and quinonphthalone. The inks can print the standard cyan, magenta, yellow and black colours and they can be stabilised for ultra violet protection. One of the issues when using these inks is that the printed colours

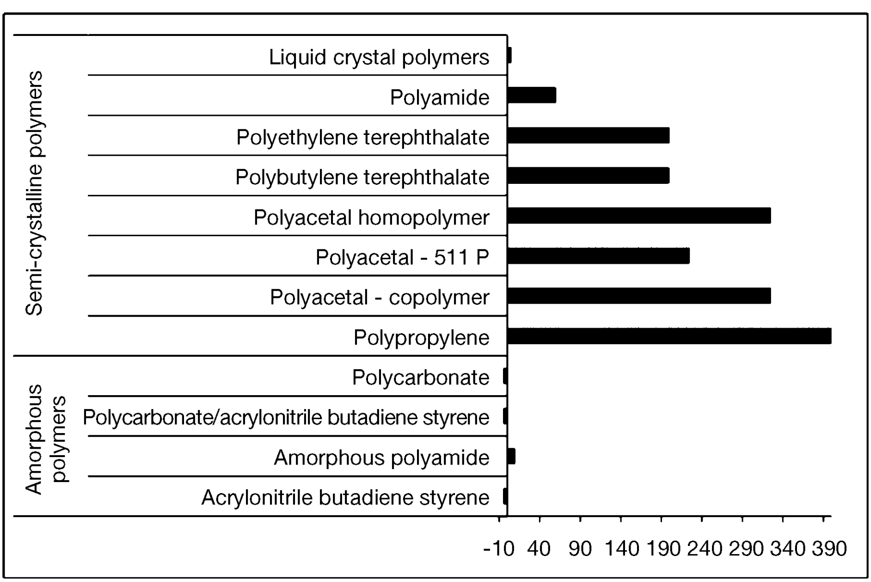

Figure 2. *Dye penetration in a range of polymers (source Adams [5])*

are translucent and therefore the base colour of the substrate is critical, and ideally needs to be white [14,15].

The data provided by Adams also shows that the penetration of the dye into amorphous polymers is somewhat limited when compared to semi crystalline materials [5]. This can affect the material selection criteria as a high level of dye penetration will improve the image robustness.

As the surface is able to withstand significant wear before the decoration is removed, component designers and manufacturers may be influenced into using semi-crystalline polymers. If however the mechanical properties of amorphous polymers are required, the end users may not select this process to decorate their components.

Another issue with dye sublimation is the robustness of the surface. There have been recorded incidents of fading images on driver's licenses in the Philippines. These licenses are produced using the D2T2, (Dye Diffusion, Thermal Transfer), process of dye sublimation, manufactured by Datacard Limited (UK) (Fareham, UK). It is believed that the licenses are subjected to "great" heat when they are stored in men's wallets and located in a trouser pocket. The images are then thermally transferred to adjacent plastic cards or surfaces. The incidence of the license failure has been recorded to be less than 0.0001% of the cards issued [16, 17].

The data presented in **Figure 2**, shows that the dyes sublimate into semi-crystalline polymers at a deeper level than the amorphous polymers. However no reason or explanation is given for this condition. This will be investigated in this research.

A high level of dye penetration in a commercial component is desirable as it will enable it to endure harsh wear and abrasive environments. This durability of the surface decoration will ensure that the component will survive its design intended lifetime.

Alternatively a low level of dye penetration into the component can bring a level of obsolescence to the component, ensuring that the surface decorated parts are replace regularly to bring additional revenue to the manufacturer of the component. This may be desirable with certain product types such as mobile phone covers which are considered to be a sacrificial part of the mobile phone.

Further knowledge of the dye penetration depth is therefore required to better inform the designers and manufacturers that may currently not use this process. This will aid them into making the correct polymer material choices, not only for the application but also to consider using the surface decoration technique.

3. EXPERIMENTAL

The following section describes the materials, equipment and testing of the experimental components.

3.1 Materials

There are two main material types. The first is the polymeric substrate materials into which the decoration is applied. The second is the dye sublimation consumable materials, used as part of the dye sublimation process. These two types of material are discussed in further detail below.

3.2 Substrate

The polymeric materials used to manufacture the substrates are listed in Table 1. These materials were selected in order to gain dye penetration depth knowledge of a range of commercially available general purpose amorphous and semi crystalline materials.

Table 1. Substrate polymers

Polymer	Manufacturer	Grade
Acrylonitrile butadiene styrene (ABS) ^{A}	ABSCOM	F350
High density polyethylene (HDPE) ^{SC}	BP	HD802GA
Polyamide (PA) ^{SC}	Vydyne	21SPC
Polybutylene terephthalate (PBT) ^{SC}	DuPont	S600F20
Polycarbonate (PC) ^{A}	Sabic	ELX 1414
Polymethyl methacrylate (PMMA) ^{A}	LG Chem	IF 850
Polypropylene (PP) ^{SC}	Bassel	HP551M
Polystyrene (PS) ^{A}	Total Petrochemicals	PS 1540
**Key: A = Amorphous, SC = Semi-crystalline*		

3.3 Consumable Materials

The dye sublimation consumable materials consist of two key types, a transfer carrier material and the dye sublimation inks, both of these are discussed below.

The Transfer Carrier (TC): The dye sublimation process developed by IDT-Systems Ltd, uses a TC which is an Amorphous Polyethylene Terephthalate

(APET) film, ranging from 160 - 200 μm thick. This film is coated with a proprietary water based release layer. The film also has a metallic layer on only one side which is used to prevent dye migration into the bulk of the film. In the three dimensional dye sublimation process the TC is firstly heated to enable it to become softened, this occurs below its glass transition temperature, (T_g), prior to being vacuum formed. Data presented by Herman, states that the T_g for APET film is 78°C [18].

Dye Sublimation Inks: The dye diffusion inks (SubliJet IQ) used during the experiments were supplied by IDT-Systems Ltd, (Dippenhall, UK) and consisted of a standard ISO CMYK colour profile [19].

3.4 Substrate Sample Preparation: Injection Moulding

The substrate polymer materials detailed in **Table 1** were prepared by means of injection moulding. This was carried out on a Battenfeld (Meinerzhagen, Germany) 110T injection moulding machine; 10 parts were produced of each material type. For the purpose of the injection moulding, the parameters for the different materials were set to the middle range of the manufacturers recommended settings; this is common practise in the injection moulding industry [20]. The experimental substrate parts were approximately 160 mm square and 3 mm thick, a photograph of the injection moulded plastic part is shown in **Figure 3**.

Figure 3. *Injection moulded plastic substrate*

3.5 Surface Decoration of the Substrate Components

The APET TC film as supplied by IDT-Systems Ltd, (Dippenhall, UK), was printed onto, using an Epson 4400 printer at a resolution of 600 dpi, with the CMYK inks. A standard CMYK test print was used for all of the substrate materials. Once the TC films were printed they were allowed to dry at room temperature.

The substrate materials were then decorated into using the dye sublimation process, the equipment used was a D6.1 transfer press, supplied by IDT-Systems Ltd (Dippenhall, UK). During processing, the substrate material was placed into the lower tray of the transfer press, the pre-printed TC was placed directly above the substrate and was held into place using a simple clamp frame. A simple schematic of the arrangement is shown in **Figure 4**.

The transfer process was set to the parameter settings shown in **Table 2**, all of the substrate materials were processed using the same parameter settings. The dye depth data presented by Adams does not provide any parameter processing data so similar comparisons cannot be made. Consequently, due to the lack of parameter settings for the different polymer types, the parameters settings selected were set to a middle range considered for the decoration of polymers.

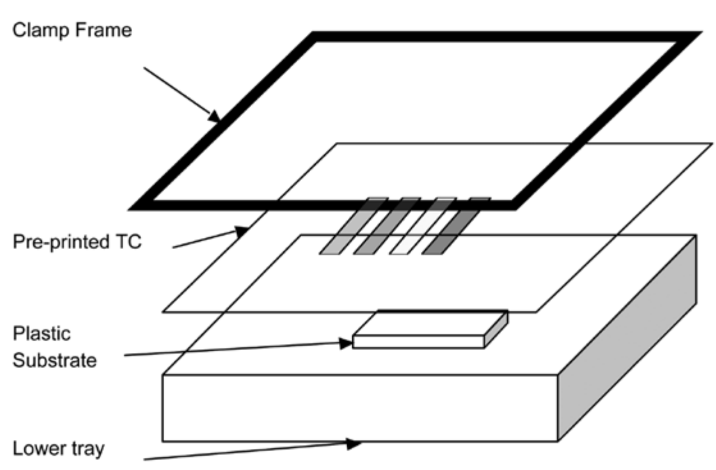

***Figure 4**. Simple schematic of the substrate and TC placed into the transfer press*

Table 2. D6.1 process parameters

Parameter	Setting	Unit
Thermo softening point	70	°C
Film soften time	5	S
Vacuum dwell	15	S
Heat temperature	175	°C
Heat time	45	S
Cooling temperature	65	°C
Vacuum pressure	-0.6 (-0.06)	Bar (MPa)

The detail of the transfer press automatic cycle is detailed below:

- Heat the TC to the “Thermo Softening Point” temperature. This temperature value is set lower than the T_g of the TC enabling the film to accurately vacuum form to the substrate.
- This temperature is maintained for the duration of the “Film Soften Time” to enable an iso-thermal condition of the TC.
- A “Vacuum Pressure” is then applied to the space in-between the TC and substrate causing the TC to vacuum form around the substrate component.
- The duration of the vacuum forming is set by the “Vacuum Dwell” time.
- Following the vacuum forming, additional heat is applied to the process until the peak “Heating Temperature” is reached. At this temperature the inks sublimate and diffuse into the surface of the component.
- The heating temperature is maintained for the “Heat Time” period, enabling all of the inks to sublimate into the surface of the substrate.
- Following this period, all of the heat is evacuated from the transfer press, to the “Cooling Temperature” enabling safe substrate removal from the transfer press.

An image of a decorated sample part is shown in **Figure 5**.

Once the experimental samples had been prepared, the individual CMYK colours were cut into small samples approximately 5 mm x 5 mm, suitable for optical microscopy. The surfaces of the samples to be viewed were then microtomed to ensure a suitable surface for optical microscopy was available. This procedure was repeated for all of the different polymer types.

***Figure 5**. Photograph of the dye sublimation decorated component*

4. RESULTS

The samples were viewed at the dye penetration surface, using an AxioScope A1 optical microscope (Carl Zeiss Ltd, Welwyn Garden City, UK). Digital images of the dye penetration were taken using an AxioCam ICC1 camera (and measurements were taken using AxioVision software.

Five dye penetration depth measurements were taken from each of the decorated colours to establish an average penetration measurement. This was repeated for each of the different substrate material types. An example of PA with the black dye penetrated into the surface of the polymer is shown in **Figure 6**. The dimensions of the dye penetration depth were taken from the top surface of the substrate to the point at which the dye has penetrated the polymer and is seen to be no longer visible.

The average values of the different CMKY dyes penetrating the different substrate materials are shown in **Figure 7** and in **Table 3**. The values shown consist of five measurements for each colour and an average calculated for each of these in turn.

5. ANALYSIS AND DISCUSSION

Table 4 is the depth of dye penetration for different polymer types, as presented by Adams [5]. Included in **Table 4** are the average values for each of the

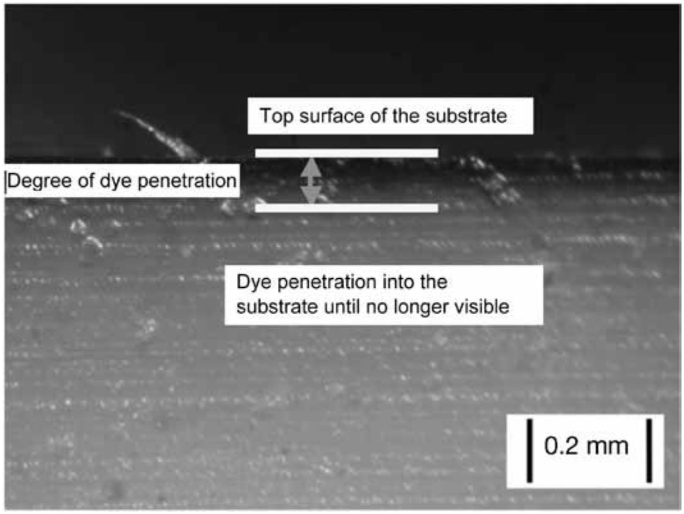

***Figure 6**. PA sample with black dye penetrated into the surface*

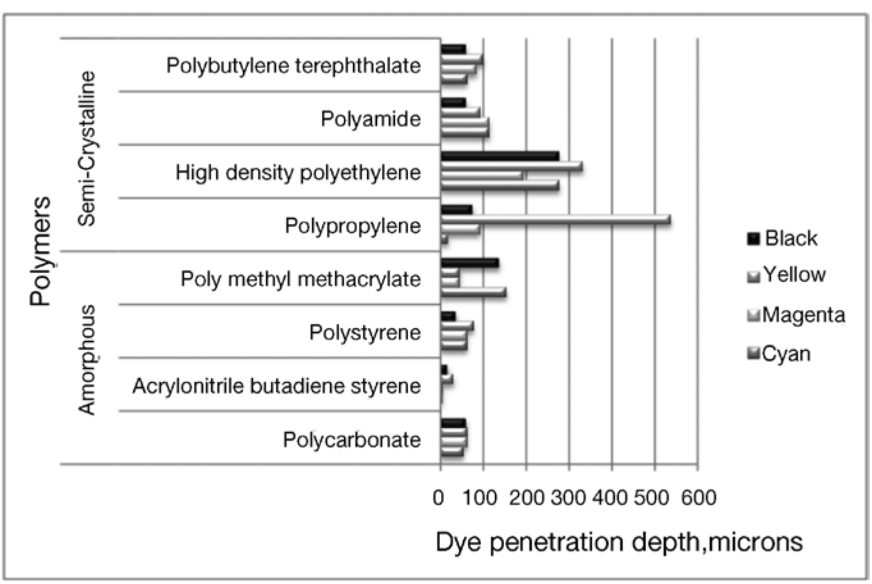

***Figure 7**. Graph of average dye penetration depths*

Table 3. Average dye depth measurements individual per material and colour, all measurements in mm

	Polymer	Cyan ± 5	Magenta ± 5	Yellow ± 5	Black ± 5	Average
Amorphous	PC	54	62	62	62	60±2
	ABS	5	6	31	19	16±5
	PS	62	62	77	38	60±7
	PMMA	154	46	46	138	96±25
Semi-Crystalline	PP	18	92	538	77	181±104
	HDPE	278	194	333	278	271±25
	PA	115	115	92	62	96±11
	PBT	62	85	100	62	77±8

Table 4. Comparison of Adam's and researchers data

Polymer	Data - Adams [5]	Data - Researcher's (average)	Difference Between Data
ABS ^{A}	+5	-16±5	21
ABS / PC ^{A}	+5	-	
HDPE ^{SC}	-	-271±25	
LCP ^{SC}	-5	-	
PA ^{SC}	-70	-96±11	26
PA ^{A}	+10	-	
PBT ^{SC}	-200	-77±8	123
PC ^{A}	+5	-60±2	65
PET ^{SC}	-200	-	
PMMA ^{A}	-	-96±25	
POM ^{SC}	-225	-	
POM – Copolymer ^{SC}	-325	-	
POM Homopolymer ^{SC}	-325	-	
PP ^{SC}	-400	-181±104	219
PS ^{A}	-	-60±7	
Key – ^{A} = Amorphous, ^{SC} = Semi-crystalline			

different polymer types as measured from the researcher's experiments, as discussed in Section 3. These values are calculated by averaging the dyes penetration depth for each of the individual colours for each of the different polymer types. The dye penetration values shown are in µm.

In **Table 4** the depth of dye penetration where a positive, (+) value is shown, is where Adams [5] intimates that there is no dye penetration, instead the dye is adding to the surface thickness of the polymer. Where a negative, (-) value is shown the dye is penetrating into the polymer. None of the experimental measurements taken from the experiments outlined in this paper resulted in an increase to the thickness to the polymer by means of addition to the sample surface.

The two sets of data show disparate values when compared to each other. Considering amorphous PC as an example; Adams shows that the dye adds 5 μm to the thickness of the polymer. The researcher's data shows a penetration depth of 60 μm, this equates to a calculated difference of 65 μm. The semi-crystalline PP material shows a 219 μm difference between the published and measured values. Other disparities in penetration of dye into the surface of the polymer are present between the materials.

The importance of this research is that when selecting this process for surface decoration of a plastic component, component designers or manufacturers may rule out this technique as a possible solution, if basing their decision on inappropriate data. Adams shows no penetration of the dye into the surface of the polymer, meaning that the decorated surface would wear very quickly with minor abrasion. DuPont go as to far as to state that the "dye does not penetrate and can be scratched off easily, when using amorphous polymers such as PC and ABS" [3].

The data differences between the researcher's findings and Adam's could be disparate based on the lack of details of the dye sublimation process parameters and the measurement process used. The lack of process parameters and settings makes comparisons between the two data sets very difficult.

The measurement errors shown in **Tables 3** and **4** highlight that a variation in the dye depth measurements taken by the researcher exists. The standard error (standard deviation/number of samples$^{1/2}$) is taken from the variation in measurement between the different colours, for each of the different polymer types. The measurement errors for ABS, PA and PP show a range which is sufficient to allow comparability between the researchers and Adams [5] dye depth measurements. PC and PBT show low levels of measurement errors.

The dye sublimation process has two key parameters, temperature and time which are selected by the user; these could directly affect the level of dye penetration into the polymer. **Table 5** shows literature results, where the different sublimation process times and temperatures are listed.

Table 5. Summary of dye sublimation temperature and times

Source	Temperature °C	Time, seconds
Adams [5]	137.7	-
Shearmur [13]	250	0.12
Sherman [21]	137.7 – 190	-
Kolourfusion [12]	190	-
Choji [22]	150 - 200	
Slark [23]	300	0.13
Wenzel [24]	182	-
Chandler [25]	185 – 232	6 - 10

The sublimation temperature data ranges from 137.7 - 300°C, which presents a vast range of operation. The literature also identifies a vast range for the time setting from 0.12 – 10 minutes. The data in **Table 4** is incomplete and therefore no real comparisons can be made of the dye penetration depth with respect to temperature and time settings.

This range of processing parameters suggests an area whereby the depth of the dye penetration can be varied in accordance to the settings used. To understand the affect of the process parameters better, further detailed experiments are required so that the impact of process parameters on the dye penetration depth can be established.

6. CONCLUSIONS

Dye sublimation is a creative technique used for the decoration of polymeric substrates. The process uses digital inkjet technology, whereby a printed image is transferred into the surface of the polymer, using a heat press. Very little academic literature is available, however a publication by Adams [5], does describe the process and the level the dyes penetrate different polymer types. The data shows that the dyes penetrate semi-crystalline polymers to a greater level than amorphous polymers types. This is an important aspect from the perspective users of this process as this could dictate the selection of the polymer being used for a particular component. Experimentation was conducted on injection moulded general purpose polymer materials. Optical microscopy established different dye penetration depths which differ greatly from those reported by Adams [5].

The previously published data indicates that the dyes barely penetrate amorphous polymers and that with some polymers the dyes sits on the surface thereby increasing the thickness of the material. The experimental results from this study show that the dyes do penetrate PC up to 65 μm more than previously reported. Semi-crystalline polymers show a considerable greater depth of dye penetration when considering the PP and HDPE polymers. However the level of dye penetration into PBT and PA polymers is comparable to the amorphous polymer types.

The results show that there are disparities between previously published data and experimental data gained from this research. Further literature reviews have highlighted a vast range in the published processing times and temperatures used in this technique. The data presented by Adams does not contain any processing information which could have affected the level of dye penetration in the different polymer types. Whilst further data has been generated with this research, it also highlights the need for further rigorous experimentation and research into this process to better understand the effect of the processing times and temperatures on the dye penetration levels and in the different polymers.

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