IN-LINE COLOR MONITORING OF POLYMERS DURING EXTRUSION USING A CHARGE COUPLED DEVICE SPECTROMETER

By

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A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science
Graduate Department of Chemical Engineering and Applied Chemistry
University of Toronto

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An inexpensive, fiber-optic equipped, charge coupled device spectrometer was used to monitor both color and residence time distributions in polyethylene melts during extrusion. A procedure involving quality control charts and spectral correction factors was developed and then used to examine the effect of screw RPM on color change-overs in a single screw extruder. A method of deriving residence time distributions from the in-line acquired reflectance spectra was derived. Dimensionless time (time/mean residence time) was shown to superimpose the residence time distribution data at the two screw speeds investigated, in accord with theory. It also superimposed L*a*b* time dependent data at the different screw speeds. Thus, the shape of these curves was unaffected by screw speed but was strongly affected by the color formulation used and the direction of the color change-over.
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1.0 INTRODUCTION

The current industrial standard of quality control for the production of pigmented polymers consists of performing critical color measurements using off-line samples. The samples collected are pressed or injected molded into a suitable physical form before the evaluation is conducted. The time delay between sample collection and evaluation can lead to large quantities of off-specification material being produced before any corrective action can be taken. Also, off-line samples can only be collected at discrete time intervals, allowing a process upset (and hence off-specification material) to pass through the system undetected. This labour intensive, discrete, off-line analysis procedure does not easily allow the implementation of an effective process control strategy.

The development of an in-line monitoring system would enable the development of automated process control by providing instantaneous, continuous feedback on the color of the product stream. However, an in-line monitoring system must meet the requirements of the harsh operating conditions within an extruder: pressures of 20 MPa and temperatures of 200°C for example.

At the beginning of this work, initial in-line color monitoring of pigmented polyolefins had been reported in the work by Calidonio [15.47]. This work observed that the color of the hot polymer was different from the same material in its cold, off-line form. The work also utilized a very bulky and expensive Vis-NIR spectrometer. The work by Sayad [49.50] used artificial neural network programming to accurately predict the color of the cooled plastic from the data obtained in-line. A new, lightweight, inexpensive charge coupled device (CCD) spectrometer was interfaced with a laptop computer to provide a portable in-line color monitoring system. The CCD spectrometer
was only briefly assessed by Sayad [49] in a series of plant trials that showed that old colored material tended to adhere to the surface of the extruder and monitoring window when the color being processed was changed [49]. The adherence of old colored material affected the performance of the color monitoring system and was only briefly examined in the undergraduate work of Gilmor [25]. This work also showed the need of a more detailed assessment of the CCD system before more testing could be conducted.

This thesis has three main objectives: (i) to assess the current capability of the CCD spectrometer to monitor color in an extruder. (ii) to develop an operating procedure for the CCD spectrometer to ensure accurate and precise measurements and (iii) to use the CCD spectrometer to investigate the effect of screw speed (RPM) on the process of color change-over in an extruder.
2.0 LITERATURE REVIEW AND THEORY

2.1 COLOR FUNDAMENTALS

2.1.1 Properties of White Light

White light is the portion of the electromagnetic spectrum, which is responsible for the observation, and measurement of color [11]. White light is not a homogenous entity but a combination of all the colors in its spectrum [30]. The spectral colors are shown in Figure 2.1 and range from 380 nm, perceived as violet, to 780 nm which is perceived as red. Each color in this spectrum is at its maximum purity that the human eye can appreciate and are therefore referred to as fully saturated, a spectral color [18].

The observation of an object's color is directly affected by the amount of light present. An insufficient amount of light results in only the size and shape of an object being determined whereas too much light results in the blinding of the observer (human or instrumental) [11].

![Figure 2.1: Visible Portion of Electromagnetic Spectrum [30]](image)

2.1.2 Scientific Definition of Color

Color can be described by specifying its hue, saturation and luminance. Hue is the attribute that specifies what type of color it is (red or blue). Saturation is defined by specifying the proportion of dominant color in the light. The saturation of a color is
decreased when it is mixed with other colors or with white light. Luminance (or brightness) refers to the total amount of light present. If a sample of uniform color is partially cast in shadow, it appears to exhibit two different colors. The darker color is a result of the decreased amount of light present, therefore lowering the luminance of the color [11].

2.1.3 Traditional Color Theories

Two different color theories can be utilized for the mixing and matching of colors.

Subtractive Color Theory: This theory is based on the inherent ability of an object to absorb certain components of white light preferentially over others. For example, an object that absorbs the shorter wavelength components of white light and reflects back the longer wavelengths will appear as a mixture of the colors associated with these reflected wavelengths. It will appear orange. If two pigments are mixed, the wavelength region of common reflectance of both pigments determines the resulting color [18].

Additive Color Theory: This theory is based on the recombination of the spectral colors in their required proportions to reproduce white light. White light can be re-created by using colors from each end of the spectrum (blue and red) along with a color from the middle of the spectrum (green). These three colors are referred to as the additive primary colors [18].

By using the additive primary colors almost every color can be matched by mixing the correct proportions of blue, green and red together until the same color is observed for both the sample and the test mixture. The amounts of each primary used to
make the match are recorded for future reference. This method of additive color
matching sets the foundation of color science and is used in color measuring equipment
[18].

2.1.4 C.I.E. Color System

The Commission International de l'Éclairage (C.I.E.) used the additive color
theory as the basis for developing a standard method for the mathematical determination
of color [18]. This method has been refined over the years and is presented in an
A.S.T.M. Standard in its current form [5].

The development of the C.I.E. color system is founded on the concept that the
additive primary colors occupy the three corners of an equilateral triangle co-ordinate
system as shown in Figure 2.2. A color is present at 100% intensity at these corners and
decrease uniformly until they are at zero intensity at any point on the opposite side. The
center of the triangle represents all three colors at equal intensity and therefore represents
white light. The sides of the triangle represent the most fully saturated colors
(determined by the particular primaries chosen) and the inside of the triangle contains all
of the various hues [18].

![Figure 2.2: C.I.E. Color Triangle [18]](image-url)
Comparison of the hues present on the sides of the triangle to their corresponding hues in the actual color spectrum were found to be not fully saturated. For example, in order to match the color of spectral blue-green, the spectral color must be diluted with a certain amount of red in order to match the blue-green on the color triangle. This is equivalent to the spectral color being located outside the color triangle. Mathematically, adding red to the test sample is quantitatively the same as subtracting red from the standard. The spectral colors are therefore located outside the color triangle, forming a locus of spectral colors. The resulting color model then allows all hues appreciated by the eye to be located within the triangle with the spectral colors being contained by this locus [18].

To avoid the use of negative numbers in the theory, the C.I.E. developed three imaginary primaries. The imaginary primaries, X, Y, and Z were chosen as supersaturated primaries so that all colors, including the spectral colors, were enveloped by this color triangle. The resulting color triangle shown in Figure 2.3 is no longer equilateral in nature [18].

![Diagram of Modified C.I.E. Color Triangle](image)

Figure 2.3: Modified C.I.E. Color Triangle [18]
Based on the development of the C.I.E. model, the values of X, Y, and Z will specify the colors hue and saturation. These numeric values are referred to as the tristimulus values of a color and form the foundation of the C.I.E. color measurement system [18].

2.1.5 FACTORS EFFECTING COLOR PERCEPTION

The color calculated based on the C.I.E. system is strongly influenced by three factors: illumination, the object (or sample) and the observer.

2.1.5.1 Illumination

Each light source possesses its own spectral power distribution, which describes the intensity of radiant energy as a function of wavelength, denoted by $S(\lambda)$. Since different light sources emit different amounts of energy, the color observed will change depending on the type of illumination used. The C.I.E. has specified the use of several different illuminants with well defined spectral power distributions. Standard illuminant "A" represents an incandescent light and standard illuminant "D65" represents daylight. The spectral power distributions of each are shown in Figure 2.4 [11.30].

![Figure 2.4: Spectral Power Distribution of C.I.E. Standard Illuminants](image)
2.1.5.2 Object

The object or sample belongs to three categories: transparent, translucent or opaque. Transparent samples absorb a portion of the light and allow the remainder to travel through the sample. Translucent samples absorb, scatter and transmit the incident light, with the scattered light being either transmitted or reflected. Opaque samples, the focus of this work, absorb and reflect the incident light. It is the reflected light that is important for color measurement [11].

During color measurement, the intensity of light reflected from the sample at each wavelength is measured and is used to generate a reflectance curve. For the numerical calculation of color, a reflectance factor is used. The reflectance factor is defined as the ratio of the intensity of light reflected from the sample to that of the intensity of light reflected from the white standard at each wavelength throughout the visible spectrum. The white standard is a material calibrated against a perfectly reflecting diffuser, which reflects all incident light symmetrically in all possible directions. By definition then, the white standard reflects 100% of the light across the spectrum. Magnesium Oxide is a suitable material for a white standard in practical color measurement [30]. The reflectance factor is denoted \( R(\lambda) \) and a representative red reflectance spectrum is shown in Figure 2.5.

![Figure 2.5: Reflectance Curve of a Red Sample](image-url)
2.1.5.3 Observer

The observer is any person or piece of equipment that perceives input of reflected light as color. Spectrometers can be utilized to detect the reflectance data and therefore occupy the role of the observer during color testing. The role of the observer is to aid in the matching of a sample’s color by indicating how much of the color primaries are required for the match. Systematic visual tests by the C.I.E. based on the sensitivity of the human eye were done in 1931 for the 2 degree visual field and in 1964 for the 10 degree visual field. The visual field corresponds to the area over which the eye views an object. The amounts of the primaries were recorded and became known as color matching functions denoted by $x(\lambda)$, $y(\lambda)$, and $z(\lambda)$ for the 2 degree standard observer and by $x_{10}(\lambda)$, $y_{10}(\lambda)$, and $z_{10}(\lambda)$ for the 10 degree standard observer [11,30]. The 10 degree standard observer, shown in Figure 2.6, is commonly used as it correlates best to the larger area that the eye integrates over when viewing a sample [14].

![Figure 2.6: Color Matching Functions of the 10 Degree Standard Observer](image)

Figure 2.6: Color Matching Functions of the 10 Degree Standard Observer [14]
2.1.6 MATHEMATICAL COLOR CALCULATION

2.1.6.1 Calculation of Tristimulus Values

The tristimulus values, X, Y, and Z are calculated using the known spectral power distribution of the illuminant, $S(\lambda)$, the reflectance factor spectrum, $R(\lambda)$, of the sample and the tabulated color matching functions, $x(\lambda)$, $y(\lambda)$, $z(\lambda)$, for the observer being used [5.11].

\[ X = \int S(\lambda) \cdot R(\lambda) \cdot x(\lambda) \approx \sum_{\lambda=380}^{780} S(\lambda) \cdot R(\lambda) \cdot x(\lambda) \]  

\[ Y = \int S(\lambda) \cdot R(\lambda) \cdot y(\lambda) \approx \sum_{\lambda=380}^{780} S(\lambda) \cdot R(\lambda) \cdot y(\lambda) \]  

\[ Z = \int S(\lambda) \cdot R(\lambda) \cdot z(\lambda) \approx \sum_{\lambda=380}^{780} S(\lambda) \cdot R(\lambda) \cdot z(\lambda) \]  

A graphical representation of the equations is shown in Figure 2.7.

Figure 2.7: Flowchart for Calculating Tristimulus Values [11]
2.1.6.2 CIELAB Color Space

Although color can be matched and compared by using the tristimulus values, there are several inconsistencies with their use. The main source of difficulty is that the human eye can distinguish a very small difference in hue when observing red but is much less sensitive to the change in hue for green. Thus a unit color difference in one color is not equivalent to a unit difference in another. The C.I.E. therefore transformed the tristimulus values to a more uniform, three-dimensional color system \[15\]. The transformation equations used for the CIELAB color space in rectangular co-ordinates \(L^*a^*b^*\) [5]:

\[
L^* = 116 \left( \frac{Y}{Y_n} \right)^{1/3} - 16 \tag{4}
\]
\[
a^* = 500 \left[ \left( \frac{X}{X_n} \right)^{1/3} - \left( \frac{Y}{Y_n} \right)^{1/3} \right] \tag{5}
\]
\[
b^* = 200 \left[ \left( \frac{Y}{Y_n} \right)^{1/3} - \left( \frac{Z}{Z_n} \right)^{1/3} \right] \tag{6}
\]

However, it is also common to report the color in polar co-ordinates which uses the \(L^*\) as above but use \(C^*\) and the hue angle \(h^*\) given below [5]:

\[
C^* = [(a^*)^2 + (b^*)^2]^{1/2} \tag{7}
\]
\[
h^* = \arctan \left( \frac{b^*}{a^*} \right) \tag{8}
\]

The variables \(X, Y, Z\) are the previously calculated tristimulus values. where \(X_n, Y_n, Z_n\) are the tristimulus values of the C.I.E. standard illuminant being used [5].
The use of the CIELAB color space, Figure 2.8, shows that $L^*$ represents the lightness of the sample with $L^* = 0$ as black and $L^* = 100$ as white. The $a^*$ value represents how green ($-a^*$) or how red ($+a^*$) a sample is and the $b^*$ value represents how blue ($-b^*$) or yellow ($+b^*$) a sample is. To completely specify a color in this system, the $L^*$, $a^*$, and $b^*$ values need to be reported [30].

![CIELAB Color Space Diagram](image)

**Figure 2.8: C.I.E. L*a*b* Color Space [14]**

### 2.1.6.3 Color Difference Formulae

When colored materials are produced they are compared to a standard as a measure of quality control. Instead of using absolute values of color, color differences are used. The total change in color, $\Delta E^*$, is used to represent the color difference in the CIE Lab color space [8].

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$ (9)
\( \Delta L^* \) is the L* of the sample minus the L* of the standard with \( \Delta a^* \) and \( \Delta b^* \) similarly defined. Typical acceptable values of \( \Delta E \) range from 0.1 to 1.0 depending on the application and colors involved. For a more detailed analysis, the individual changes in L*, a* or b* can be monitored and used in specifications [14].

2.1.7 Concentration from Color: The Beer-Lambert Law

Once the reflectance factor of a sample has been obtained, the absorbance and concentration of the color species can be determined. The Beer-Lambert Law relates the reflectance factor \( R(\lambda) \), the absorbance \( A(\lambda) \), the path length \( b \), the molar absorptivity \( \varepsilon(\lambda) \), and the concentration \( C \) of a sample at a particular wavelength [28].

\[
\log[1/R(\lambda)] = A(\lambda) = \varepsilon(\lambda) b C
\] (10)

The color of the sample is indicated by the location of the maximum wavelength for reflectance. For example, if the maximum reflectance occurs at approximately 510nm the sample will be probably green in color [28].

2.2 PRACTICAL COLOR MEASUREMENT

2.2.1 Spectrometers and Accessories

For practical color measurement, a spectrometer is used. The spectrometer must be able to acquire the spectrum of a sample over the entire visible wavelength range, provide good signal to noise ratio, have a rapid rate of data acquisition and provide all
this at the lowest possible cost [11]. In previous work by F. Calidonio (1996) a conventional NIR Systems spectrometer was used for in-line color monitoring but this system is large and very expensive. These drawbacks and the slow data acquisition through DOS-based software made this option unattractive to the polymer processing industry [15].

To overcome these problems, a color monitoring system using a small, inexpensive charge coupled device (CCD) spectrometer (Model: S1000) manufactured by Ocean Optics Inc. (Dunedin, FL) was assembled in the work by M.H. Sayad (1998) [49]. The assembled system uses a light source (CIE Standard Illuminant A. Model: LS1), a bifurcated fiber optic reflection probe, the CCD spectrometer and a laptop computer with Windows based software for color monitoring. The bifurcated probe consists of two legs: the illumination leg containing six illumination fibers and the read leg that contains the single read fiber [42]. The two legs join together to form one probe tip containing all seven fibers, the read fiber in the middle surrounded by the six illumination fibers therefore allowing the single probe to both illuminate and collect the reflected light from the sample [49].

The reflected light is transmitted to the CCD spectrometer through the read leg of the fiber. Once inside the CCD spectrometer, as illustrated in Figure 2.9, a spherical mirror (1) is used to collimate the divergent light exiting the fiber. A diffraction grating (2) is then used to decompose the light into the individual wavelengths. The light is then focused onto the one-dimensional CCD array (4) by the use of a second spherical mirror (3). The projected image of the reflected light is then sent to the Windows program for data analysis by an A/D card. The resulting system was only briefly tested during a plant
trial at G.E. Plastics (Sayad 1998) and a more detailed assessment is one of the major goals of this work [49].

Figure 2.9: CCD Spectrometer [49]

2.2.2 Accuracy of Measurements

2.2.2.1 Influence of the Equipment

Color measurements can only be compared when measured under the same conditions and by the same equipment geometry [4]. A change in the equipment or the viewing geometry will result in different color values being reported. When using the same equipment a standardized procedure is needed to help ensure accurate and reproducible measurements. Ocean Optics Inc. recommends a thirty minute warm up period for both the S1000 CCD spectrophotometer and the LS1 light source [42]. This warm up procedure is required to ensure that the spectral output of the LS1 is constant and that any residual signal in the S1000 has been removed. Only after these defined
warm up periods will accurate black (0% reflectance) and white (100% reflectance) references be obtained.

2.2.2.2 Influence of the Sample

The sample being observed can affect the reported color measurement in several ways. A sample with non-uniform color as a result of poor pigment dispersion will result in a large spread within the data when the sample is read at multiple random spots. The surface of the sample can also affect the measurement. A glossy surface will exhibit a large specular reflection component compared to a matte surface. Figure 2.10 shows the difference in reflection of a matte surface to a smooth, glossy surface. The industry standard is to measure the color of a sample in a diffuse measurement (ie. gloss is excluded by the conditions used). The colors of pigments employed today in polymers are often sensitive to changes in temperature (ie. the pigments are thermochromic) [11].

Figure 2.10: Reflectance of Matte versus Glossy Sample [11]
2.2.2.3 Control Chart Theory

One of the most widely used tools for statistical quality control is a control chart. They are based upon the fact that any process contains a certain amount of inherent variability that is not removable. Control charts allow us to determine the magnitude of this inherent variability and provides a reference for comparison at any point in time. First the variable to be studied is chosen and measured several times. The grand mean of the measurements ($\bar{x}$) is calculated along with standard deviation ($\sigma$) and the Upper and Lower Control Limits are calculated as [10]:

$$\text{Upper Control Limit} = \bar{x} + 3\sigma$$

$$\text{Lower Control Limit} = \bar{x} - 3\sigma$$

An example of a control chart is given in Figure 2.11 below.

![Figure 2.11: A Typical Control Chart](image-url)
It is customary to use limits that are in the form of \( \pm \frac{3\sigma}{\sqrt{n}} \), where \( n \) is the number of observations in each sample. For color monitoring, once the calibration has been conducted, the number of observations within a sample only gives information on the noise within a calibration and not the effect of calibration itself. Therefore observations of size \( n=1 \) per calibration and multiple calibrations are used to accurately quantify the calibration effect for the color monitoring system.

To utilize the power of the control charts established rules have been generated to help determine if the process is becoming unstable. To aid the rules, control charts often display the \( \pm 1\sigma \) and \( \pm 2\sigma \) values along with the Upper and Lower control limits. The major rules indicating that the system is becoming unstable are: 1) One point falls outside of the control limits. 2) Two out of three points fall between the \( 2\sigma \) limit and the control limit on the same side of the centerline. 3) Four out of five points fall between the \( 1\sigma \) limit and the control limit on the same side of the centerline. 4) Eight consecutive points fall on one side of the centerline [21].

It is emphasized that the control limits established are not equivalent to the design specifications or engineering tolerances. They simply indicate that the process is operating within its natural limits. Therefore it is possible that an "in-control" process can produce "off-specification" parts [10].

### 2.2.2.4 Corrective Measures for Spectral Data

Numerical correction for known errors in spectral data can improve the accuracy and reproducibility of the results. Methods have been developed which are applicable to the reflectance factors obtained and work well for correcting errors in the photometric
scale (reflectance value) or wavelength scale but not for differences in the measurement technique, such as different equipment or viewing geometry [30].

If an instrument incurs an error in its zero setting (black reference), the result is a constant offset throughout the spectrum. The true reflectance value, \( R_d(\lambda) \), is then related to the measured reflectance value, \( R_m(\lambda) \), by a constant \( B_0 \).

\[
R_d(\lambda) = R_m(\lambda) + B_0
\]  

(13)

If the instrument incurs an error when obtaining the reflectance factor of the white standard (100% setting), the result is a constant percentage error throughout the spectrum. The cause of an error in the white spectrum is usually attributed to an older white standard being used in the calibration procedure. The true reflectance value is related to the measured reflectance value by a constant percentage \( B_1 \).

\[
R_d(\lambda) = R_m(\lambda) \left[ \frac{100 + B_1}{100} \right]
\]  

(14)

Corrective measures for a) an error in the wavelength scale consisting of a simple shift of all the wavelengths in the same direction, b) a non-linearity in response of the photo-detector or its associated electronic circuits or c) an instrument possessing too large a spectral bandwidth have been published but were not required in this work [30].
2.3 IN-LINE COLOR MONITORING

2.3.1 Probe and Interface Designs for In-line Monitoring

The measurement of polymeric properties "in-line" requires that the equipment be able to withstand the harsh operating conditions of the typical extrusion process. Temperatures of greater than 200°C and pressures of 20 MPa and harsh chemical compounds are common operating conditions [48.49].

2.3.1.1 In-line Monitoring Probe Design

The designs of probes that are able to withstand these conditions have gained an increased amount of attention and research. Wand probes have been designed to monitor polyol production and have been rated for pressures up to 6.8 MPa and temperatures up to 200°C [51]. Transmission probes used to monitor the additive concentration during polymer extrusion has been developed by Schirmer and Gargus for pressures up to 20.4 MPa and temperatures up to 300°C [48.51].

The work by Hansen and Khettry describe the development and subsequent use of a modified composite probe for the in-line monitoring of polymer blends using Near Infrared spectroscopy. The composite probe involved the construction of a protective housing which would accommodate a standard transmission probe. The protective housing was comprised first of a nickel-iron alloy tube on which a sapphire window was bonded. The nickel-iron alloy tube was then brazed to a stainless steel housing to complete the exterior shell. A gap between the interior walls of the protective housing and the optical probe allowed the circulation of cooling air [27].
The issue of fouling is often cited as an objection to in-line spectroscopy. The work by Sohl has shown that there have been no fouling effects over four years of runtime work with dozens of different materials and probe designs. Probes can be designed to use the hydrodynamic shear forces of the flowing medium to remove the old material that may accumulate on the probe's viewing surface and therefore do not foul irreversibly. Sohl has mentioned that fouling effects are observed due to oxidation if a probe is removed with hot melt still adhering but can be eliminated by cleaning or replacement of the probe tip [53].

The main drawback to most of these designs is that they are dedicated systems. They are able to measure only one property at a time and are often immersed in the environment they are monitoring. If the optical property for monitoring is changed, or if a probe is damaged, the existing probe must be replaced for another one more suited for the application. This usually requires the process to be shut down in order to make the change [48].

2.3.1.2 In-Line Monitoring Interface Development

To overcome the limitations of a dedicated probe system, the development of multi-functional interfaces which allows the use of a variety of optical probes have been developed in the research done at the University of Toronto and are detailed in an article published in Applied Spectroscopy. Volume 53 [48]. Essentially, these interfaces consist of a hole with a sapphire window at the bottom. Sapphire was chosen as the window material of choice due to its excellent mechanical, thermal and optical properties [33,48]. The holes and window are designed large enough to accommodate a wide variety of
optical probes that range in both size and application. Adjustment collars are readily used to secure the smaller diameter probes in position when placed in a larger hole [48.49].

This design not only protects the optical probes from the harsh operating environment of the extruder but also allows the replacement or switching of probes without interference to the process. Two relevant designs of the interface are discussed [48.49].

Melt-in-Barrel Interface: This interface design places the probe hole and sapphire window in the barrel of the extruder, usually located between the screw tip and the die. This design is easily adapted to industrial extruders as it only requires modifications to the existing extruder without the manufacturing of any extensive parts. Although it was used infrequently at the University, it was utilized in the work by M.H. Sayad [49] in industrial plant trials at G.E. Plastics (Cobourg, ON). Recently, concerns have been raised about the low velocities that occur near the window's surface if it is located in a large diameter flow channel. This and the possible effect of polymer pigment adhesion to the interface window were observed in the work by Sayad [49].

Melt-at-Die Interface: This interface is a rectangular block of dimensions: roughly 41mm in length and 76mm in width and height. It is made of stainless steel that is bolted to the end of the extruder's die. The interface matches the location and number of die holes so that, when attached, it effectively lengthens the die. The die strand to be monitored has two cylindrical holes perpendicular to it, which can accommodate the
sapphire windows, copper gaskets and the hollow cylindrical collars used for sealing the system. Sapphire windows that are 2 millimeters thick and that are angled at 45 degrees are placed so that they protrude into the flow channel by 0.5 mm. This protrusion into the flow is to prevent the formation of any stagnant layers. This interface design was utilized extensively in work at the University and detailed diagrams are shown in Figures 2.12a and 2.12b [48]. The unmonitored die hole was modified by making it roughly 1.3cm wide for one quarter of the channel length to allow the use of flow regulators. This section is threaded and allows flow regulators the length of the die to be screwed into the die with different internal diameters (from 0 to 3.18mm) to allow for different flow rates between the die holes.

![Diagram of Melt-at-Die Interface](image)

**Figure 2.12a: Cross Section of Melt-at-Die Interface**
All Dimensions in Millimeters
The work performed in collaboration with Colortech Inc. (Brampton, ON) resulted in plant trials using a melt-in-barrel design. Two dedicated color probes were designed but were never utilized. Appendix B details the designs of the two color probes.

2.3.2 Overview of In-Line Color Monitoring

Presently there is not much published literature on the topic of in-line color monitoring. Other methods, such as on-line monitoring of color, have been investigated in the industry of continuous textile dying. For this system a spectrometer with a probe for color measurement was situated above the surface of the fabric by 15-20 mm. The probe is then moved across the width of the fabric in order to obtain the measurement. It was found that with this setup many factors such as: ambient light, distance between the measuring head and fabric, fabric surface unevenness, the fluttering of the fabric.
vibration of the measuring head and the atmospheric contents and/or contaminants can all adversely effect the color measurement [32].

In the work by Calidonio in collaboration with Colortech Inc. [15.47], a twin screw extruder was used with a Vis-NIR spectrometer to assess the ability of monitoring color in-line by utilizing the melt-at-die interface. A series of colored masterbatches (green and gray) of polyolefins were extruded without dilution at various operating conditions. The extrusion runs were designed to investigate whether the Vis-NIR spectrometer could measure color in-line and if successful, whether or not it could discern when “off-specification” product was being extruded [15.47].

The results showed that the in-line color monitoring system could successfully differentiate between the good and bad samples for most of the colors provided at an extrusion temperature of 150°C. The in-line system also had no trouble in distinguishing between the two levels of luminance in the samples [15.47].

The effects of increasing the extrusion melt temperature on one of the gray samples resulted in a change in both the a* and b* color co-ordinates. The a* co-ordinate tended to increase into the red region whereas the b* color co-ordinate tended to increase into the yellow region when measured in-line. Off-line analysis of the samples showed that the gray samples reverted back to their original color once cooled to room temperature. The conclusion was that a reversible thermochromic phenomenon was taking place in the titanium dioxide (TiO₂) pigment present in the gray color masterbatch formulation. Subsequent heating and cooling tests were carried out on several red formulations and later on the pure red pigment itself. These tests clearly showed a reversible thermochromic change in the a* and b* color co-ordinates as well. The high
temperatures resulted in lower $a^*$ and $b^*$ values which increased in magnitude as the sample cooled. Visual tests confirmed this, with the change in hue from a dark brick red to a bright red color during these experiments being observed [15.47].

Color differences were observed when the in-line measurements were compared to their corresponding off-line measurements. As previously mentioned, changes to the samples temperature and/or physical state will effect the perceived color due to changes in the intensity of the reflected light. This work clearly showed the need to develop a correlation between the two measurements [15.47].

In the work by Sayad [50] the in-line and off-line measurement data obtained by Calidonio [15.47] were used to develop a model for predicting the off-line color values from the experimentally obtained in-line measurements. Three mathematical methods were assessed: principal component regression (PCR), partial least squares (PLS) and an artificial neural network (ANN). The resulting predicted values by each method were plotted together along with the true values. The ANN method provided superior results in comparison to the PCR and PLS methods as significant deviations were present for these two methods in the corresponding data plots. Furthermore a plot of residuals, calculated as the difference between the known and the predicted values of the color coordinates, rarely deviated from zero for the ANN method whereas large deviations were present for the other two methods [50].

With a method of color prediction now developed, further work by Sayad [49] was focused on reducing the cost of the current in-line color monitoring system. Although the Vis-NIR spectrometer worked admirably in the work by Calidonio it was both expensive and bulky. An inexpensive fiber-optic-assisted charge-coupled device
spectrometer (Ocean Optics Inc., FL) was interfaced with a laptop computer for in-line color monitoring. After developing the system, it was briefly assessed in a series of plant trials in co-operation with G.E. Plastics Inc [49].

A transition piece that modeled the melt-in-barrel interface design was connected after the screw and before the die. A total of three colored polycarbonate resins were extruded at 270°C and measured in-line. The in-line results varied with time but moved towards values indicative of their respective color. Visual observations through a second sapphire window, not in use for color monitoring, showed that the older material was only slowly leaving the surface of the interior barrel wall and sapphire window. This observation was confirmed by observing different die strands that showed different colors amongst them. It was deemed that the old color tended to “hang-up” on the interior surfaces, an unsatisfactory result [49] that led to this work.

2.4 IN-LINE MONITORING RESPONSE TIME

Response time of the monitoring system strongly depends upon how long material remains at the surface of the sapphire window. At one extreme, material may arrive at the window and not be replaced during the run. In that case, the shear stresses on the material at the surface are insufficient to overcome the attraction of the material to the window. The response time is then so long that the monitoring system would be useless for process control. It is therefore important that the surface renewal of material at the window be sufficiently rapid that changes in the color of the stream can be rapidly discerned by the monitoring system.
Reducing adherence of material to the window can be done by decreasing the work of adhesion of the material [19] to the window and by increasing the shear stress on the material [64]. Studies of the former can involve various window surface treatments for example and this work is currently in progress here. As will be seen below, an added complication is that elastic effects in addition to interfacial surface energies, may contribute to causing a "no slip" condition at the wall.

In this thesis, emphasis is entirely upon examining the effect of a change in shear stress obtained by changing extruder screw speed (i.e. the shear rate). When the extruder screw speed is changed, the time dependent color co-ordinate values obtained during a color change over at the new speed will differ from those at the old speed. What is being observed is the combined effect of adherence of material to the window and axial mixing (i.e. residence time distribution) in the extruder. The first of these topics is examined by considering shear rate at the window and reviewing what is known about slip at the wall. The second is dealt with by deriving a residence time distribution from the reflectance spectra instead of color co-ordinates. The characteristics of the experimental residence time distributions as it changes with screw rpm can then be compared to a well known theoretical residence time distribution. A side benefit of deducing the residence time distribution is that, in addition to providing information on detector response time and window surface renewal, it can be used for other purposes (such as quantifying the speed of a change over in terms of colorant concentration).
2.4.1 Shear Rate at the Surface of the Window

For the polymers employed here, the well known power law adequately describes the relationship between shear stress and shear rate [22]:

$$\tau = k\dot{\gamma}^n$$  \hspace{1cm} (15)

where $\tau$ is shear stress, $\dot{\gamma}$ is shear rate and $k$ and $n$ are constants with $n$ being less than unity for our pseudoplastic fluids. The viscosity, $\eta$, is then [22]:

$$\eta = k\dot{\gamma}^{n-1}$$  \hspace{1cm} (16)

Melt Flow Index (MFI) is also used as a crude single point measure of polymer viscosity. The MFI is the number of grams of polymer that flows out of the required piston/die apparatus in a standardized 10-minute interval. Materials that have a high viscosity have as a result low MFI values [9].

For capillary and slit flow, equations for the shear stress and shear rate at the wall of the flow channel have been developed [16,20]. For channels of unusual cross section, the derivation of the relevant equations requires numerical calculation of the equations of motion. Kozicki et al. [34] simplified the method by using two geometric constants to relate the flow rate to the shear rate at the wall. and the work by Miller [38] simplified it further by relating the shear rate to only one geometric constant. The average wall shear rate ($\dot{\gamma}$) is related to the volumetric flow rate (Q) by the cross sectional area ($A_c$).
hydraulic diameter \((D_h)\), and the characteristic shape factor \((\Omega)\) which is dependant only on the flow channels geometry.

\[
\dot{\gamma} = \frac{Q\Omega}{2A_D D_h}
\]  

(17)

The values of \(\Omega\) are tabulated in the literature [38] along with equations for its calculation for numerous geometries. Substitution of the shape factor for circular or slit cross sections into Equation (17) results in the expected equation for each flow channel. For a flow channel of rectangular cross-section (width = a, height = b), the shape factor is calculated using the following relation.

\[
\Omega = \frac{24}{\left[\left(1 - 0.354(b/a)\right)\left(1 + (b/a)\right)\right]^2}
\]  

(18)

The fundamental equation for the flow rate through a single screw extruder with a cylindrical die hole is presented below. The nomenclature used and its relation to the physical dimensions of the extruder are presented in Appendix C. The total flow rate out of an extruder, assuming zero leakage flow, is given by:

\[
Q_t = \sqrt{\frac{\pi DH W \cos \theta}{2\left(1 + \frac{2WLH^c}{\pi R^3}\right)}}
\]  

(19)
The only variable in Equation (19) is the value N, as all of the other parameters are constants that relate the physical geometry of the extruder screw and barrel. The value of N is referred to as the rotational speed, usually given in RPM. The total flow rate \( Q_T \) is directly proportional to N and therefore doubling the RPM results in doubling the total flow rate from the extruder [9].

2.4.2 "Slip" at the Wall

A common assumption for fluid flow is that the velocity of the fluid at the wall of the tube is zero, commonly referred to as the "no-slip" condition [13]. Under this condition, the material at the wall surface would take an infinite amount of time to be removed from the system. However, previous work by C.Gilmor has shown that during a color change-over experiment, the new material was visibly seen replacing the old material at the surface of the window with a definite end to the change-over process [25].

Galt and Maxwell investigated the nature of the velocity profiles for polyethylene melts in circular and rectangular tubes using particle tracer techniques. Their results indicated that the relative velocity of the polymer melt at the wall need not equal the assumed zero value. While they did observe some zero velocities at the wall, the majority of the velocities had a finite value at the wall. They suggested that the polymer melt undergo a behavior termed "stick-slip flow" which is caused by melt elasticity. The mechanism of this flow is depicted in Figure 2.13 and occurs in a boundary annulus located between the tube wall and the remaining flow [23].
The melt sticks to the wall at surface B. The melt is then sheared by the flow of the bulk polymer at surface A and deforms elastically. The melt at surface B then "slips" and catches up with surface A, thereby removing the elastic strain. This procedure is repeated down the length of the tube and the resulting velocity profiles therefore varied greatly close to the wall and became more uniform/constant in the center of the tube where plug flow occurs [23].

Confirmation of non-zero wall velocities have been reported for linear low density polyethylene in thin slits [52], in circular conduits [29] and for high density polyethylene in rectangular conduits [2]. The onset for wall slip to occur is reported to be around a critical wall shear stress in the range of 0.1 to 0.3 MPa [57].

Several models have been postulated for estimating the occurrence of slip and the slip velocity: if the apparent wall shear rate is plotted against 1/R (radius) for a fixed shear stress and temperature for capillary flow, and against 1/H (height) for slit flow. the
slope of the resulting straight line is four or six times the slip velocity for capillary and slit flow respectively. A horizontal line indicates that no slip flow is occurring [16,20]. A slip velocity model in the form of a power law equation has been proposed but it has been found to be valid for only a limited range of shear stress [54]. Currently more complex models have been postulated to estimate the slip velocity of polyethylene melts in capillary flow. The model presented below by Hatzikiriakos [29] for the slip velocity ($u_s$) incorporates rate activation theory, similar to theory used in models by Stewart et al. [54] and Lau et al. [35].

$$u_s = \frac{2\alpha KT}{Nh} e^{-E_{B}^\tau_{w}} \sinh\left(\frac{E}{RT} \left(\frac{\tau_{w}}{\tau_{c}} - 1\right)\right)$$  \hspace{1cm} (20)

In the above model $K$ is the Boltzman's constant, $h$ is Planck's constant. $R$ is the molar gas constant, $T$ is the absolute temperature, $\Delta G_0$ is the energy required for a polymer molecule to change its position. $E$ is the minimum energy that the shear stress must overcome for slip flow to occur. $N$ is the number of macromolecules bonded to various wall sites and $\tau_w$ and $\tau_c$ are the wall and critical wall shear stress [29].

Although slip at the wall can occur, it is important to know what factors may affect it so wall slip can be promoted in desirable processing operations. Recently the effects of the material of construction and surface roughness on slip flow have been investigated using LLDPE. Results showed that the wall slip velocities increased with decreasing surface roughness and that the wall slip velocities were the highest for stainless steel in comparison to those for copper, aluminum and glass. Wall slip was
observed at wall shear stress values as low as 0.04 MPa for stainless steel as it exhibited relatively low values for the work of adhesion [19]. Xing and Schreiber [64] made use of a fluoropolymer coating on the internal surfaces of the extruder’s die that resulted in the promotion of slip flow for the processing of Dowlex 2045 LLDPE, the same material used in this thesis. The fluoropolymer preferentially wets the die surface and interacts very weakly with the LLDPE, therefore acting as a lubricant between the polymer and stationary phase [64].

2.4.3 Residence Time Distribution

The Cumulative Residence Time Distribution Function, \( F \), is the fraction of the exit stream that is of age time \( t \) or less (i.e. of age between 0 and \( t \)) and is bounded by the values of zero and one \((0 \leq F(t) \leq 1)\). This constraint is due to the fact that no element of age \( t=0 \) can leave before time zero and that all fluid elements that entered at \( t=0 \) are assumed to eventually exit. The \( F(t) \) curve starts at a zero value and increases to a value of unity as a function of time. The \( F(t) \) distribution is also the probability that a fluid element that entered at time zero has exited by time \( t \) [36,40].

The opposite of the \( F(t) \) distribution is the Washout Residence Time Distribution Function, \( W(t) \). Here \( W(t) \) is defined as the probability that a fluid element that entered the vessel at time zero has not left at time \( t \). The \( W(t) \) function is bounded by zero and unity as is the \( F(t) \) function, but begins at a value of unity and decreases to zero with increasing time [40]. Thus:

\[
W(t) = 1 - F(t) \quad (21)
\]
The above residence time distributions can be expressed in terms of dimensionless time \( \theta \), calculated as time \( t \) divided by the mean residence time \( \bar{t} \) [40].

\[
\theta = \frac{t}{\bar{t}} \tag{22}
\]

The definitions for the above residence time distributions are now given in terms of the dimensionless time below [40]:

\[
F(\theta) = F(t) \tag{23}
\]

\[
W(\theta) = W(t) \tag{24}
\]

The mean residence time for any arbitrary flow is easily obtained from the \( F(t) \) curve as indicated in Figure 2.14 [36].

\[
\text{Area} = t
\]

Figure 2.14: Calculation of \( \bar{t} \) from the \( F(t) \) Distribution [36]
2.4.4 Determining \( F(t) \) and \( W(t) \) from In-line Reflectance Spectra

The Beer Lambert Law can be used to determine the necessary concentrations from the series of reflectance spectra obtained in-line during a color change over. There were two major issues: a variety of different pigments and dyes may be present in each color concentrate and the absolute value of the initial and final concentrations were unknown. To overcome these issues we assume that all of the different colorants in a specified concentrate would behave as one additive. Also, we realized that the initial and final concentrations of these two additives, although unknown, were constant with time. Thus, as shown in Appendix A, we could solve the Beer Lambert law for the ratio of concentrations rather than individual concentrations. The concentration ratios also represented the \( F(t) \) and \( W(t) \) residence time distributions and could be substituted accordingly into the equations. The final set of equations obtained were:

\[
\int_{\lambda_1}^{\lambda_2} A_1 d\lambda = W_1(t) \int_{\lambda_1}^{\lambda_2} A_{1in} d\lambda + F_1(t) \int_{\lambda_1}^{\lambda_2} A_{1out} d\lambda \tag{25}
\]

\[
\int_{\lambda_1}^{\lambda_2} A_2 d\lambda = W_2(t) \int_{\lambda_1}^{\lambda_2} A_{2in} d\lambda + F_2(t) \int_{\lambda_1}^{\lambda_2} A_{2out} d\lambda \tag{26}
\]

2.4.5 Theoretical Residence Time Distribution for a Single Screw Extruder

The work of Tadmor and Klein present the cumulative residence time distribution, \( F(t) \), for single screw extruders. The set of equations presented below are used to generate the \( F(t) \) curve with more detailed descriptions of the variables presented in
Appendix C [56]. The variable of \( y/H \) represents the position of a fluid particle in the \( y \)-direction between the surface of the screw and the barrel (distance \( H \)).

\[
F(t) = F\left(\frac{y}{H}\right) = \frac{1}{2} \left[ 3 \left(\frac{y}{H}\right)^2 - 1 + \left(\frac{y}{H} - 1\right) \left[ 1 + 2 \frac{y}{H} - 3 \left(\frac{y}{H}\right)^2 \right]^{1/2} \right] \quad (27)
\]

\[
t = \frac{l}{3V_s \left(1 + \frac{Q_p}{Q_d}\right) \sin \theta \cos \theta} \left[ \frac{3 \frac{y}{H} - 1 + 3 \left[ 1 + 2 \frac{y}{H} - 3 \left(\frac{y}{H}\right)^2 \right]^{1/2}}{\frac{y}{H} \left[ 1 - \frac{y}{H} + \left[ 1 + 2 \frac{y}{H} - 3 \left(\frac{y}{H}\right)^2 \right]^{1/2} \right]} \right] \quad (28)
\]

The RTD is calculated by solving Equations (27) and (28) simultaneously and is dependent on the fluid particle's position \( y/H \). As the variable \( y/H \) is increased, only one distinct pair of \( t, F(t) \) values are calculated and when plotted generate the RTD shown in Figure 2.15.

![Figure 2.15: Theoretical F(t) Distribution for a Single Screw Extruder [56]](image-url)
These equations assume no-slip at the wall of the extruder and they therefore predict that infinite time will pass for \( F(t) \) to equal one when evaluated at the position of \( y/H = 1 \) (the surface of the barrel). However it is known that the material at the surface is eventually removed [56].

Examination of Equation (28) shows that the RTD of a single screw extruder is dependent on a single dimensional group (time units),

\[
\frac{l}{3V_s\left(1 + \frac{Q_n}{Q_d}\right) \sin \theta \cos \theta}
\]

whose variables are all a function of the extruder geometry and operating conditions, defined in Appendix C. Changing any of these variables, such as the rotational frequency of the screw (RPM) will only change the time scale of RTD and not its characteristic shape because the dimensional group is merely a multiplying factor within Equation (28). As Figure 2.15 shows, the shape is determined by the fluid particle's position \( (y/H) \). Therefore a universal RTD for a single screw extruder can be plotted if dimensionless time is used. As an alternative to using the mean residence time in the calculation of dimensionless time, the minimum residence time can also be used [56].
3.0 EXPERIMENTAL

The experimental work involved three main areas 1) in-line CCD spectrometer assessment, 2) development of an in-line operating procedure using off-line monitoring methods, and 3) examination of the effect of RPM on color change over. These areas are examined in turn in the following sections.

3.1 IN-LINE CCD SPECTROMETER ASSESSMENT

The CCD spectrometer was assessed in-line by a series of experiments with small changes in the color of the hot polymer melt. The purpose of these experiments was to assess the quality of the color monitoring system as is and to identify any sources of error.

3.1.1 Materials

Table I lists all of the materials used for the in-line assessment. All pigmented polymers were supplied through Colortech Incorporated (Brampton, ON).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>14287-18: Red</td>
<td>65.5%: 20 MI LLDPE</td>
</tr>
<tr>
<td></td>
<td>4%: TiO2</td>
</tr>
<tr>
<td></td>
<td>14.8%: Red Pigment</td>
</tr>
<tr>
<td></td>
<td>15.7% Fillers and additives</td>
</tr>
<tr>
<td>Dowlex 2045</td>
<td>1 MI LLDPE</td>
</tr>
<tr>
<td>Heliogen Blue</td>
<td>68.8-69.0%: 7-16 MI LLDPE</td>
</tr>
<tr>
<td></td>
<td>30%: KRONOS 2073</td>
</tr>
<tr>
<td></td>
<td>1.0-1.2%: Heliogen Blue</td>
</tr>
</tbody>
</table>
3.1.2 Extrusion and In-Line Monitoring

A ¾” Brabender single screw Extruder (Type: 2503-GR-8, Model: 1629) with a length to diameter ratio of 25:1 was used for all in-line testing at the University. The extruder was equipped with four heating zones, three in the barrel and one in the die. The extruder temperature was set at 190°C in all four zones for all experiments.

The CCD spectrometer (S1000) was interfaced to the extruder using a bifurcated fiber optic reflection probe (ZR400-7-VIS/BX) that was inserted into the multi-functional interface attached to the die of the extruder. Each scan provided a single instantaneous reflectance spectrum. The resulting in-line L*a*b* color co-ordinates were calculated using the C.I.E. Standard Illuminant A and the 10-degree observer angle. Figure 3.1 shows a schematic of the experimental set-up.

![Figure 3.1: In-Line Color Monitoring Experimental Set-Up](image)

Mixing Assessment: Mixtures of pigmented Red polymer and Dowlex 2045 linear low density polyethylene (LLDPE) ranging from the composition of 1/99 to 5/95 red polymer/LLDPE by weight inclusive were prepared and extruded at 10 RPM. Each experimental run was 10 minutes in duration with in-line reflectance data acquired in six-
second time intervals. The experimental work was performed on three separate days. The one and five weight percent mixtures occupied the first two days whereas the remaining mixtures were extruded on the third day in a randomized order.

Day to Day Variation: Six additional experimental runs were performed using the 5/95 Red/LLDPE mixture. Two runs per day were conducted for the duration of 10 minutes with the second run commencing three minutes after the completion of the first run. The mixture was extruded at 10 RPM with in-line reflectance data collected in six-second time intervals.

Colortech Plant Trials: A ¾" single screw extruder (Farrel Corp. Model: CP-23) with length to diameter ratio of 10:1 was used in a series of subtle color changes in blue pigmentation. The sapphire window used for protecting the reflectance probe was located in the barrel of the extruder, between the screw tip and the die, and was flush mounted with the interior wall. The color monitoring system was the same as that used in work at the University.

A set of four experimental runs were performed that involved changing the concentration of the blue pigment, in 0.1% increments, from 1.0% to 1.2% and then returned to the original 1.0% formulation. The temperature profile in the barrel was maintained at 165°C with the die temperature set at 190°C. All runs were extruded at a screw speed of 50 RPM and were 30 minutes in duration. The in-line reflectance data were collected in 18-second time intervals for the duration of the run.
3.1.3 Off-line Monitoring

During the Colortech Plant Trial experiments, samples were collected in two-minute time intervals for subsequent off-line analysis. The sample pellets were formed into color plaques by first passing them through a 2-roll mill and by pressing them using a manual hot press at a temperature of 150°C. The resulting color plaques were analyzed as part of the Sensitivity Assessment detailed in Section 3.2.2.3 and Section 4.2.3.2.

3.2 DEVELOPMENT OF AN IN-LINE OPERATING PROCEDURE USING OFF-LINE MONITORING METHODS

The results of the In-Line CCD Spectrometer Assessment indicated the need to develop a specific procedure tailored to ensure both precision and accuracy. This off-line evaluation focused on three aspects: reproducibility (random error), systematic error and sensitivity.

3.2.1 Materials

For all experiments investigating random and systematic error, color chips provided from Colortech were used. The color chips were blue, green, red and yellow and their formulations were not available. A book of color standards, known as the Pantone Book in the color industry, was used to examine the sensitivity of the system. The color standards used in this experiment are given in Table II with their formulation. The color plaques made from the samples obtained during the Colortech Plant Trials were also used to assess the system's sensitivity.
Table II: Pantone Color Standards used in Sensitivity Assessment

<table>
<thead>
<tr>
<th>Pantone Color Standard</th>
<th>Pigment Formulation (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue 2905U</td>
<td>Pro Blue (3.9)</td>
</tr>
<tr>
<td></td>
<td>Ref. Blue (2.3)</td>
</tr>
<tr>
<td></td>
<td>Trans. Wt. (93.8)</td>
</tr>
<tr>
<td>Blue 2915U</td>
<td>Pro Blue (7.8)</td>
</tr>
<tr>
<td></td>
<td>Ref Blue (4.7)</td>
</tr>
<tr>
<td></td>
<td>Trans. Wt. (87.5)</td>
</tr>
<tr>
<td>Green 337U</td>
<td>Pro Blue (4.7)</td>
</tr>
<tr>
<td></td>
<td>Yellow (1.6)</td>
</tr>
<tr>
<td></td>
<td>Trans. Wt. (93.7)</td>
</tr>
<tr>
<td>Green 338U</td>
<td>Pro Blue (18.8)</td>
</tr>
<tr>
<td></td>
<td>Yellow (6.2)</td>
</tr>
<tr>
<td></td>
<td>Trans. Wt. (75.0)</td>
</tr>
<tr>
<td>Red 1777U</td>
<td>Red 32 (25.0)</td>
</tr>
<tr>
<td></td>
<td>Trans. Wt. (75.0)</td>
</tr>
<tr>
<td>Red 1787U</td>
<td>Red 32 (50.0)</td>
</tr>
<tr>
<td></td>
<td>Trans. Wt. (50.0)</td>
</tr>
<tr>
<td>Yellow 3935U</td>
<td>Yellow (9.08)</td>
</tr>
<tr>
<td></td>
<td>Pro Blue (0.07)</td>
</tr>
<tr>
<td></td>
<td>Trans. Wt. (90.85)</td>
</tr>
<tr>
<td>Yellow 3945U</td>
<td>Yellow (34.7)</td>
</tr>
<tr>
<td></td>
<td>Pro Blue (0.3)</td>
</tr>
<tr>
<td></td>
<td>Trans. Wt. (65.0)</td>
</tr>
</tbody>
</table>

3.2.2 Off-Line Monitoring

All measurements involved using the in-line color monitoring system following 60-minute and 30 minute warm up periods for the light source and spectrometer respectively (in accordance with manufacturer’s recommendation). Diffuse reflectance data were collected and the CIE L*a*b* color coordinates were calculated using the C.I.E. Standard Illuminant A and the 10-degree standard observer. For all experiments using the color plaques, a plaque holder was used to ensure that the same spot of the color plaque was measured for all experimental work. The probe and probe holder were
aligned using markings to ensure that probe alignment remained constant. The order of the plaques was randomized for each experiment.

3.2.2.1 Random Error Experiment

**Number of Scans/Temperature Effect:** Each color plaque was scanned from 10 to 40 times, in increments of 10, at a frequency of three-second time intervals. Each scan provided a single instantaneous reflectance spectrum. A thermocouple was placed between the color plaque and the fiber optic probe to estimate the increase in temperature incurred by the color plaque for the duration of the experiment.

**Signal Averaging:** The number of instantaneous reflectance spectra to be averaged per scan was set at 1, 2, 5, 10, 20, and 40. Each color plaque was scanned a total of five times for each of these settings.

3.2.2.2 Systematic Error Experiments

For each of the following systematic and sensitivity experiments, the data was collected in five-second time intervals with each scan being the average of 20 instantaneous reflectance spectra.

**Calibration Effect:** The color monitoring system was warmed up and calibrated five different times to simulate five different working days. After each calibration, the color plaques were scanned a total of five times.

**Drift Evaluation:** All of the color plaques were scanned a total of five times every hour during the course of a nine-hour day after the initial calibration was performed.
3.2.2.3 Sensitivity Assessment

**Pantone Book Experiments:** A total of eight color standards, two from each color, were scanned a total of 35 times on the same location.

**Colortech Plant Plaques:** The plaques from the first experimental run, Blue 1.0% to Blue 1.1% were scanned 35 times on the same location. A second experiment measured only the first and last plaques of this run using 35 random location.

### 3.3 EFFECT OF RPM ON COLOR CHANGE-OVER

The in-line color monitoring system was used to investigate the effect of RPM on color change-over using experiments involving the "flushing" or "new addition" of a color concentrate to the extruder.

#### 3.3.1 Materials

Table III lists the all of the materials used in the RPM assessment. All materials except the LLDPE carrier resin from Dow Chemicals were supplied through Colortech Incorporated.

#### 3.3.2 Extrusion and In-Line Monitoring

The experimental set-up used for the RPM assessment was identical to the in-line CCD spectrometer assessment set-up (Figure 3.1). The extruder temperature was set to 190°C in all four heating zones. A 5/95 mixture by weight of pigmented polymer (blue or red) concentrate/LLDPE was used and the LS1 light source was warmed up for a period of five hours previous to monitoring.
Table III: Materials used in the RPM Assessment

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>14287-18: Red</td>
<td>65.5%: 20 MI LLDPE 4%: TiO2 14.8%: Red Pigment 15.7%: Fillers and Additives</td>
</tr>
<tr>
<td>16102-08: Reflex Blue</td>
<td>59.6%: 7.5 MI LDPE 6.6%: TiO2 0.5%: Red Pigment 32%: Blue Pigment 1.3%: Additives</td>
</tr>
<tr>
<td>Dowlex 2045</td>
<td>1 MI LLDPE</td>
</tr>
<tr>
<td>10851-67: Purge</td>
<td>Proprietary Formula</td>
</tr>
</tbody>
</table>

Shear Rate Evaluation: The extruder was randomly set to various RPM settings in the range of 2 to 24 (inclusive) in multiples of two. The extruder was allowed to run for five minutes before the collection of mass flow rate samples was initiated for a Red/LLDPE mixture. For each RPM setting, five flow rate samples were collected over a five-second time interval.

Change-Over Experiments: The in-line work consisted of performing a complete 2-level factorial experiment replicated once for the variables “screw speed” (RPM) and “color change-over direction” for each of the two color pigment formulations. The direction of change-over was determined by changing the mixture in the feed hopper from the 5/95 mixture of pigmented polymer concentrate/LLDPE to an industrial off-white purge material and then returning again only to the 5/95 mixture in the hopper. The new color was added when the old material had decreased in the feed hopper to the point of exposing the surface of the screw. In-line monitoring was initiated at that time. Each in-line reflectance measurement was the average of 20 instantaneous measurements.
using the 10-degree standard observer and C.I.E. standard illuminant A. Tables IV and V
give the experimental conditions for the red and blue change-over experiments respectively.

Table IV: Experimental Conditions for Red/Purge Change-Over

<table>
<thead>
<tr>
<th>Run #</th>
<th>Direction</th>
<th>RPM</th>
<th>Scan Rate (s)</th>
<th>Monitoring Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Red to Purge</td>
<td>10</td>
<td>27</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>Purge to Red</td>
<td>10</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>Red to Purge</td>
<td>20</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>Purge to Red</td>
<td>20</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Red to Purge</td>
<td>10</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>Purge to Red</td>
<td>10</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>Red to Purge</td>
<td>20</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>Purge to Red</td>
<td>20</td>
<td>12</td>
<td>20</td>
</tr>
</tbody>
</table>

Table V: Experimental Conditions for Blue/Purge Change-Over

<table>
<thead>
<tr>
<th>Run #</th>
<th>Direction</th>
<th>RPM</th>
<th>Scan Rate (s)</th>
<th>Monitoring Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Blue to Purge</td>
<td>10</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>Purge to Blue</td>
<td>10</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>Blue to Purge</td>
<td>20</td>
<td>18</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>Purge to Blue</td>
<td>20</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Blue to Purge</td>
<td>10</td>
<td>33</td>
<td>55</td>
</tr>
<tr>
<td>6</td>
<td>Purge to Blue</td>
<td>10</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>Blue to Purge</td>
<td>20</td>
<td>21</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>Purge to Blue</td>
<td>20</td>
<td>12</td>
<td>20</td>
</tr>
</tbody>
</table>

3.3.3 Off-Line Monitoring

Once in-line monitoring was initiated, off-line samples were collected at regular
one-minute intervals for the duration of the experimental run. These samples provided
qualitative insight into the in-line monitoring performance. However, radial non-
uniformity of color precluded meaningful quantitative analysis.
4.0 RESULTS AND DISCUSSION

4.1 IN-LINE CCD SPECTROMETER ASSESSMENT

4.1.1 Mixing Assessment

The in-line L*a*b* color co-ordinates as a function of red concentrate loading are shown in Figure 4.1a to 4.1c inclusive. Figure 4.1a shows that the L* co-ordinate, a measurement of the amount of light present, decreases with increasing red pigment concentration from 2wt% to 5wt%. The in-line values also became more constant with increasing concentration. These results were expected as the red hue is darker at higher concentrations. It is also seen that the L* value for 1wt% red is roughly equivalent to the values obtained for the 5wt% mixture which is contrary to the expected results. It was discovered that the differences between calibrations performed on the different days of experimentation resulted in this observed offset.

Figure 4.1b shows the a* color co-ordinate response due to increasing red concentration with the 1wt% mixture and 5wt% mixture having the lowest and highest in-line a* values respectively. a* increases as expected since it is a measure of the amount of red present in the sample. Figure 4.1b also shows a decrease in the high frequency noise as the amount of red concentrate was increased because the higher concentrations tended to conceal inadequate mixing of the colorant by the extruder.

Figure 4.1c shows the b* color co-ordinate response as a function of red concentrate loading. The level of high frequency noise is greatest for the 1wt% mixture but is relatively constant for the remaining mixtures. Closer examination of the data shows that the 1wt%, 4wt% and 5wt% mixtures exhibit a positive slope as a function of
Figure 4.1a: $L^*$ as a function of Red Concentrate Loading

Figure 4.1b: $a^*$ as a function of Red Concentrate Loading

Figure 4.1c: $b^*$ as a function of Red Concentrate Loading

Figure 4.2a: $L^*$ Residuals for 1wt% Red

Figure 4.2b: $L^*$ Residuals for 3wt% Red

Figure 4.2c: $L^*$ Residuals for 5wt% Red
time. Furthermore, the 4wt%, 2wt% and 3wt% show a slow removal of this behaviour with the 3wt% mixture possessing a relatively constant value for the duration of the experiment. The order in which the 2wt% to 4wt% mixtures were conducted correspond to this observed decrease in the apparent slope of the graph as the 4wt% and 3wt% were the first and last run of the day respectively. It thus appeared that the time that the experiment was conducted on a given day affected not only the slope of the b* coordinate but its relative value as well.

To observe the effect of concentrate loading on the level of low frequency noise exhibited in the data, residuals and standard deviations of the L*, a* and b* values obtained were calculated by the method of successive differences (Appendix D, Equation D-3). The coefficients of variation based on 100 samples, expressed as a percentage and calculated using Equation D-4, are presented in Table VI as a function of concentrate loading. Figures 4.2a to 4.2c show the L* co-ordinate residuals for 1wt%, 3wt% and 5wt%. All three residual graphs have the same scale on the vertical axis.

Table VI: Coefficient of Variation as a Function of Red Concentrate Loading

<table>
<thead>
<tr>
<th>Response Variable</th>
<th>1wt%</th>
<th>2wt%</th>
<th>3wt%</th>
<th>4wt%</th>
<th>5wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>0.089</td>
<td>0.034</td>
<td>0.029</td>
<td>0.030</td>
<td>0.061</td>
</tr>
<tr>
<td>a*</td>
<td>2.406</td>
<td>0.707</td>
<td>0.553</td>
<td>0.551</td>
<td>0.542</td>
</tr>
<tr>
<td>b*</td>
<td>2.706</td>
<td>0.640</td>
<td>0.576</td>
<td>0.714</td>
<td>0.756</td>
</tr>
</tbody>
</table>

Examination of Table VI shows that for both the L* and b* co-ordinates the coefficient of variation decreased from 1wt% to 3wt% but increased slightly at 4wt% and 5wt%. This trend is also exhibited in the three residual plots for the L* color co-ordinate. The coefficient of variation did continue to decrease with increased pigmentation for the
a* co-ordinate but the values were relatively constant from 3wt% to 5wt%. Figures 4.2a to 4.2c also show that the noise in the data is a result of random variations in the system, due to the lack of observable trends in the calculated residuals. Similar results were obtained for the residual plots of the a* and b* color co-ordinates.

To gain further insight into the results observed in this experiment, a series of runs using only the 5wt% red colorant in LLDPE was conducted. Their results are detailed in the following section.

4.1.2 Day to Day Variation

The in-line L*a*b* color coordinates for the day to day variation experiments are presented in Figures 4.3a to 4.3c inclusive. Each figure shows the two runs (a data set) conducted each day for three days along with the results of the 5wt% red mixture obtained from the Mixing Assessment for comparative purposes for a total of seven individual runs.

The day to day variation exhibited by the L* and a* color co-ordinates are shown in Figures 4.3a and Figure 4.3b respectively. Although there is large spread in the in-line values obtained for the four sets of data, there is considerable overlap within any one data set (two runs on the same day) for both color co-ordinates. This clearly shows the effect of the individual calibrations performed at the beginning of each day of experimentation.

Figure 4.3c shows the effect of the day to day variation on the b* color coordinate. Although roughly the same degree of spread is seen for all seven experimental runs, careful examination of the data shows that the b* value for the second run is always larger in magnitude than the b* value of the first run of the day. The slope in the b*
Figure 4.3a: Red L* Day to Day Variation

Figure 4.3b: Red a* Day to Day Variation

Figure 4.3c: Red b* Day to Day Variation

Figure 4.4a: Day1-Run1 a* Residuals

Figure 4.4b: Day1-Run2 a* residuals
value is also reduced in the second run to the point that the \( b^* \) value is relatively constant in comparison to that of the first run of the day. This trend indicated the need for an increased warm up time previous to data collection.

To further investigate the need of increased warm up time, residuals and standard deviations were calculated by the method of successive differences. Table VII presents the standard deviations for the \( a^* \) color co-ordinate calculated based on twenty data point intervals and the entire data set for both runs performed on Day 1. Figures 4.4a and 4.4b show the \( a^* \) residuals calculated for Day1-Run1 and Day1-Run2 respectively.

<table>
<thead>
<tr>
<th>Data Range</th>
<th>Time (minutes)</th>
<th>Day1-Run1</th>
<th>Day1-Run2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-100</td>
<td>0-10</td>
<td>0.2018</td>
<td>0.0476</td>
</tr>
<tr>
<td>1-20</td>
<td>0-2</td>
<td>0.4040</td>
<td>0.0464</td>
</tr>
<tr>
<td>21-40</td>
<td>2-4</td>
<td>0.0544</td>
<td>0.0541</td>
</tr>
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<td>41-60</td>
<td>4-6</td>
<td>0.0521</td>
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<td>61-80</td>
<td>6-8</td>
<td>0.0489</td>
<td>0.0407</td>
</tr>
<tr>
<td>81-100</td>
<td>8-10</td>
<td>0.2019</td>
<td>0.0531</td>
</tr>
</tbody>
</table>

The standard deviations calculated using the entire data set show that the second run has a lower standard deviation by an order of magnitude. This calculation is verified by the examination of the residual plots in Figures 4.4a and 4.4b which clearly show that the \( a^* \) residuals for the first run are higher over the first 100 seconds and for the upset that occurs just before 500 seconds into the run. This sudden change in the \( a^* \) residual for Day1-Run1 is also evident in Figure 4.3b. However the residual plots seem to indicate that, excluding these regions, the residuals are of equal magnitude. The standard deviations calculated by using twenty data point intervals clearly show that after the first 100 seconds, the noise within the data sets are roughly equivalent for the data point range...
of 21 to 80. Very similar and consistent results were obtained for both the L* and b* residual plots and their calculated standard deviations for the day to day variation results.

4.1.3 Colortech Plant Trials

The in-line L*a*b* results from the Colortech Plant Trials involving subtle changes in blue pigment concentration are presented in Figures 4.5a to 4.5c inclusive. All four experimental runs are included in each figure and therefore represent the change in blue pigment concentration from 1.0% to 1.2% in 0.1% increments and back to the original 1.0% formulation.

Figure 4.5a: L* Colortech Plant Trials

Figure 4.5b: a* Colortech Plant Trials

Figure 4.5c: b* Colortech Plant Trials
Figure 4.5a presents the change in the L* color co-ordinate. It was expected that the L* value should have decreased from an initial steady state to a minimum value when the 1.2% blue formulation was being run and then return to the original steady state value. Figure 4.5a shows that the L* color co-ordinate does decrease in value but does not reach a true steady state for the 1.2% blue formulation. nor does it return to the original starting value. Also, in each of the four individual runs a large fluctuation in the in-line values is evident.

Figure 4.5b shows the change in the a* color co-ordinate. The a* value was expected to decrease with increasing blue pigment concentration and to behave in a manner similar to the L* color co-ordinate. The in-line data shows the same type of fluctuation that occurred in the L* color co-ordinate and only shows a possible increase for the last two experimental runs.

The change in the b* color co-ordinate is presented in Figure 4.5c. The b* color co-ordinate should have decreased (become more negative) in value as the blue pigment concentration increased. Not only did the opposite of this trend occur but the same type of fluctuation seen in the L* and a* in-line data was present in the b* in-line data.

Evaluation of the in-line L*a*b* color co-ordinates indicates unsuccessful monitoring of the subtle changes in the blue pigment concentration. Possible causes for these results were: 1) The in-line color system was unable to distinguish between such small changes in color. 2) The window, which was flush mounted to the interior wall of the extruder, was located in a region of stagnant/insufficient flow. 3) The material adhered irreversibly to the window surface.
4.1.4 Summary of the In-Line CCD Spectrometer Assessment

The in-line assessment revealed the CCD results to be unreliable. High frequency random noise appeared in some runs and a day to day variation in response was also evident. Furthermore, even the ability of the instrument to discern between given differences in color was in question. A new operating procedure that addressed these concerns needed to be developed.

4.2 DEVELOPMENT OF AN IN-LINE OPERATING PROCEDURE USING OFF-LINE MONITORING METHODS

The development of the operating procedure focused on three aspects: reproducibility (random error), systematic error and sensitivity. Each are discussed individually in the following sections. A representative result (one color only) for each of the following experiments is presented and discussed in detail as similar results were obtained for all colors.

4.2.1 Random Error Experiments

4.2.1.1 Number of Scans/Temperature Effect

It is known that color pigments used in polymer processing are often thermochromic in nature in that they can change color with a change in temperature. To ensure that the use of the supplied color chips introduced no bias in the measurements for the development of the operating procedure, the effect of changing the number of scans was first investigated. Increasing the number of scans introduces a temperature effect by
increasing the duration of illumination due to the fiber optic probe being placed directly above the surface of the color chip and could introduce localized temperature fluctuations.

The resulting standard deviations with 95% confidence limits were calculated and plotted as a function of the number of scans performed. Figures 4.6a to 4.6c present the calculated standard deviations for the $L^*a^*b^*$ color co-ordinates of the yellow color chip (note the change in the color co-ordinate scale on the $b^*$ plot). Examination of these plots shows that the standard deviation (within a color co-ordinate) remains unchanged as the number of scans increases. Based on these results, any number of scans less than 40
could be used without adversely effecting the error associated with the experimental data collected in future experiments using these color chips.

4.2.1.2 Signal Averaging

To reduce the noise within a set of measurements the method of signal averaging was employed. The goal of this experiment was to determine the optimal value of individual spectra to average per scan without exceeding equipment limitations. The number of scans (n) for each data point was fixed at five and the number of spectra (N) to average per scan were increased from one to forty. The resulting standard deviations with 95% confidence limits were calculated and compared to their estimated values.

The estimated values of standard deviation (σ) were obtained by using the value of σ(N=1) and dividing by \( \sqrt{N} \) for each subsequent value of N. Therefore the estimated value of σ(N=5) is \( \sigma(N=1)/\sqrt{5} \) and the estimated value of σ(N=40) is \( \sigma(N=1)/\sqrt{40} \).

The experimentally obtained standard deviations were compared to their estimated values by plotting them on the same graph. The L*a*b* standard deviations as a function 1/\( \sqrt{N} \) for the green color chip are given in Figures 4.7a to 4.7c respectively (the value of N increases to the left, solid line represents estimated values of σ). These figures show that the experimentally obtained values of the standard deviation generally tend to decrease with increasing values of N as predicted by the estimated values. While the expected decreasing trend is evident, the graphs are not as well behaved as was hoped. Not only is there some overlap when considering the 95% confidence limits but some of the experimentally determined standard deviations exceed both their estimated
Figure 4.7a: L* Standard Deviation Versus Number of Spectra per Scan

Figure 4.7b: a* Standard Deviation Versus Number of Spectra per Scan

Figure 4.7c: b* Standard Deviation Versus Number of Spectra per Scan

Figure 4.8a: Green Reflectance for N = 2

Figure 4.8b: Green Reflectance for N = 20

Figure 4.8c: Green Reflectance for N = 40
values and the value of when $N=1$ (as seen in the $b^*$ plot: Figure 4.7c). This result is partially due to the re-calibration that must be conducted for each value of $N$ (dictated by valid equipment and measuring techniques).

To aid in the selection of the optimal value of $N$, representative reflectance curves were extracted and compared for each value of $N$. The reflectance curves corresponding to the green color chips for $N=2$, $N=20$ and $N=40$ are presented in Figures 4.8a to 4.8c respectively. Drastic improvements in the quality (smoothness) of the reflectance curve is evident across the entire visible spectrum when $N$ is increased from 2 to 20 and this was true for all color chips examined. The green reflectance curve does show some minor improvements when $N$ is increased from 20 to 40 but the change in $N$ was unnoticeable in the reflectance curves for the remaining colors. This observation, along with the fact that the experimentally determined standard deviation values remained relatively unchanged for $N \geq 20$ resulted in the selection of $N = 20$ for all future experiments. The in-line system could obtain the average of 20 spectra per scan in less than two seconds and provided a standard deviation in the order of $10^{-2}$ for the $L^*a^*b^*$ color co-ordinates.

4.2.2 Systematic Error Experiments

4.2.2.1 Calibration Effects

As seen in the previous experiments (Mixing Assessment, Day to Day Variation and Signal Averaging) the in-line color monitoring system proved to be sensitive to the calibrations that were performed before each experiment. Therefore a control chart
Figure 4.9a: Blue L* Control Chart

Figure 4.9b: Blue a* Control Chart

Figure 4.9c: Blue b* Control Chart

Figure 4.10a: Red L* Control Chart

Figure 4.10b: Red a* Control Chart

Figure 4.10c: Red b* Control Chart
methodology was implemented to monitor the validity of the calibrations performed from day to day. The control charts generated help to determine the magnitude of the inherent variability that is not removable from the system: which is the calibration of the Black and White references before experimentation. The control charts also help monitor the validity of the measurements throughout an experiment as they provide a reference for comparison at any point in time. The control charts for the L*a*b* color co-ordinates of the blue and red color chips are presented in Figures 4.9a to 4.9c and Figures 4.10a to 4.10c respectively. Each of the control charts were generated using the procedure outlined in Section 2.2.2.3.

4.2.2.2 Drift Evaluation

An evaluation of the color monitoring system by measuring the color chips every hour was conducted over the period of a nine-hour workday. The resulting changes in the L*a*b* color co-ordinates as a function of time for the yellow color chip are presented in Figures 4.11a to 4.11c respectively: the L* color co-ordinate decreased with time whereas both the a* and b* color co-ordinates increased with time. However the scale on the y-axis for all three color co-ordinates shows that although the absolute value of the color co-ordinates changed, the percentage change was generally small. The L* color co-ordinate changed less than 1% over the course of the nine hour evaluation period (note the expanded scale on the y-axis) and the a* and b* color co-ordinates changed less than 2% and 5% respectively. The relative magnitude of the variation was usually less than 5% in the L*a*b* color co-ordinates for the remaining color chips.
The drift evaluation results also showed that the color co-ordinates reached a new steady state five hours into the evaluation, as seen in both the a* and b* color co-ordinate graphs (Figures 4.11b and 4.11c). Comparison with representative reflectance curves at each hour showed that the reflectance curves appeared quite constant after the five hour marker with most of the fluctuations in the reflectance curves during the first four hours located in the low wavelength region (380-420nm). Although the relative changes in the L*a*b* color co-ordinates was generally less than five percent and only small changes were seen in the reflectance curves, a five hour warm up for the LS1 light source was implemented for future experimental work.
4.2.3 Sensitivity Assessment

4.2.3.1 Pantone Book Experiments

The reflectance curves for Green 337U and Green 338U from the Pantone Book are presented in Figure 4.12 with their respective formulations presented in Table II. Both of the green reflectance curves are smooth across the entire spectrum and show a strong maximum peak at approximately 525nm, the middle of the green region of the visible electromagnetic spectrum (Figure 2.1). Table VIII presents the calculated means and standard deviations of the L*a*b* color co-ordinates for both green samples.

Table VIII: Pantone Green Experimental Color Co-ordinate Values

<table>
<thead>
<tr>
<th>Color</th>
<th>Data Measure</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green 337U</td>
<td>Mean</td>
<td>76.885</td>
<td>-30.894</td>
<td>4.436</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.011</td>
<td>0.013</td>
<td>0.019</td>
</tr>
<tr>
<td>Green 338U</td>
<td>Mean</td>
<td>67.067</td>
<td>-40.286</td>
<td>5.607</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.025</td>
<td>0.013</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Comparison of the reflectance curves to their respective formulations and their calculated color co-ordinates shows that the color monitoring system could detect the difference between the two colors. As the amount of pigments responsible for the green colorant (blue and yellow) increased, the calculated a* value became more negative indicating more green was present in the sample. As the amount of the white pigment was reduced in the formulation the calculated L* value decreased indicating the sample was darker in hue. This reduction in the L* color co-ordinate is clearly seen in Figure 4.12 as the reflectance curve for Green 338U is of lower intensity across the spectrum than for that of Green 337U.
Hypothesis testing based on the sample means of the color co-ordinates for the two green samples were conducted based on the method outlined for large sample sizes in Appendix D with the Null Hypothesis being that the difference between the two means was zero (H₀: μ₁-μ₂ = 0). The z test statistic was calculated at 95% confidence and compared for the critical value for a two-tailed test. If the absolute value of the test statistic is greater than the critical value then the Null Hypothesis can be rejected. Results of the Hypothesis Test for the Pantone Green samples are given in Table IX.

**Table IX: Hypothesis Test Results for Pantone Green Samples**

<table>
<thead>
<tr>
<th>&quot;z&quot; value</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test statistic</td>
<td>2101.5</td>
<td>3031.4</td>
<td>-284.6</td>
</tr>
<tr>
<td>Critical value</td>
<td>1.959961</td>
<td>1.959961</td>
<td>1.959961</td>
</tr>
</tbody>
</table>

The test statistic for all three color co-ordinates is much greater than the critical value calculated at the 95% confidence level and hence the Null Hypothesis can be rejected for each color co-ordinate. In fact the test statistic value is so much greater than the critical value that the Null Hypothesis could be rejected at a confidence level greater
than 99.99%. This results indicates that the mean values of the L*a*b* color co-ordinates for Green 337U and Green 338U are different and therefore the color monitoring system had no trouble in distinguishing between the color of the samples. Similar results were obtained for the other colors measured, however these color differences are still relatively large in the color industry. The next experiment examines the systems ability to detect subtle color differences off-line.

### 4.2.3.2 Colortech Plant Trial Color Plaques

The off-line samples obtained were pressed into color plaques and measured 35 times in the same location. The resulting L*a*b* color values are presented in Figures 4.13a to 4.13c as a function of time for the change in blue pigment concentration from 1.0% to 1.1%. These figures show a fair degree of scatter in the data and no observable trends. It was uncertain as to whether the true color difference had been masked by the use of the 2-roll mill in the making of the color plaques or if the system could not distinguish the color difference. A second set of L*a*b* data was collected using only the first (blue pigment concentration = 1.0%. "B1") and the last plaques of the run (blue pigment concentration = 1.1%. "B1.1"). Both plaques were again scanned 35 times but each in different, random locations. Hypothesis testing performed at the 95% confidence level with the Null Hypothesis being that the difference between the two means was zero (Ho: \( \mu_1 - \mu_2 = 0 \)) was conducted on the resulting L*a*b* means. The results are presented in Table X.
Table X: Color Plaque Results based on Randomized Locations

<table>
<thead>
<tr>
<th>Color Plaque</th>
<th>Data Measure</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>Mean</td>
<td>63.308</td>
<td>-36.888</td>
<td>-41.359</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.357</td>
<td>0.3994</td>
<td>0.415</td>
</tr>
<tr>
<td>B1.1</td>
<td>Mean</td>
<td>63.11</td>
<td>-37.04</td>
<td>-41.533</td>
</tr>
<tr>
<td></td>
<td>Standard deviation</td>
<td>0.383</td>
<td>0.353</td>
<td>0.325</td>
</tr>
<tr>
<td>Hypothesis</td>
<td>test statistic</td>
<td>2.235233</td>
<td>1.678752</td>
<td>1.962469</td>
</tr>
<tr>
<td>Testing</td>
<td>Critical value</td>
<td>1.959961</td>
<td>1.959961</td>
<td>1.959961</td>
</tr>
<tr>
<td></td>
<td>Minimum sample size</td>
<td>29</td>
<td>51</td>
<td>37</td>
</tr>
</tbody>
</table>

Comparison of the experimental color co-ordinate values shows that the L* value for plaque B1 is larger in magnitude and is therefore lighter in hue than plaque B1.1 which reflects the decrease in the carrier resin and the increase in blue pigmentation. The
increase in blue pigmentation is observed in the b* value which has decreased from plaque B1 to B1.1 indicating that the sample has indeed become more blue. Both of these experimental observations match with the expected theoretical results.

The hypothesis testing results show that Null hypothesis can be rejected at the 95% confidence level for both the L* and b* color co-ordinates (it is noted that the test statistic for b* is marginally greater than the critical value). The test statistic for the a* color co-ordinate is less than the critical value and therefore the Null Hypothesis must be accepted at the 95% confidence level. These results do show that the color system can distinguish the difference between the color plaques by the use of large, randomized samples. Statistical methods were used to determine the minimum number of samples needed for the color system to distinguish between the color plaques for all three color co-ordinates. This method used a value of 0.05 for both the Type I and II errors and with results shown in Table X. Since all three color co-ordinates are required to determine the color of a sample the largest value (a*) dictates that a minimum of 51 scans are needed to distinguish between the color plaques for this subtle change in blue pigment concentration.

If a process upset in color, of the same magnitude as described for these blue pigments, occur it is unlikely that the system will be able to gather enough scans to accurately distinguish between them. The color system has demonstrated its ability to determine large color differences, and is applied to this situation in the next phase of the work, but the system may be at its limitation for such small color differences in-line.
4.2.4 Summary of Development of an Operating Procedure

The results outlined by the previous experiments led to the development of the operating procedure currently used for in-line color monitoring. The operating procedure is detailed in Appendix E and the critical characteristics it incorporates are:

i. a warm up time of 5 hours for the light source (greatly exceeding the vendor recommendation of 30 minutes)

ii. accurate placement of the spectrometer probe for both off-line and in-line measurements

iii. the use of 20 averaged spectra per reflectance scan obtained for both off-line and in-line measurements

iv. the establishment and use of statistical control charts for monitoring the accuracy of the calibrations performed at the beginning of each experiment

v. the use of spectral correction factors (Equations 13 and 14) to remove any errors that may have occurred in the photometric scale (reflectance value)

vi. an off-line test method to assess whether post calibration drift is occurring within the monitoring system

vii. an off-line test method to assess the sensitivity of the system to discern small color differences

4.3 EFFECT OF RPM ON COLOR CHANGE-OVER

With reliable results now obtainable with the new operating procedure work progressed to investigate the effect of extruder screw speed (RPM) on the process of color change-over in an extruder.
4.3.1 Shear Rate Evaluation

The mass flow rate samples of the 5/95 by weight red/LLDPE mixture were used along with Equations (17) and (18) to calculate the mean wall shear rate within the monitored die hole of the transition piece. The flow channel was approximated by a rectangular cross section of dimensions $a = 3.18\text{mm}$ and $b = 2.18\text{mm}$ with $n = 0.72$. As shown in Figure 4.14 and Table XI, the wall shear rate increases linearly from 36 to $69\text{s}^{-1}$.

![Figure 4.14: Mean Wall Shear Rate with 95% Confidence Limits](image)

Table XI: Calculated Mean Wall Shear Rate and Mean Wall Shear Stress

<table>
<thead>
<tr>
<th>Extruder RPM</th>
<th>Mean Wall Shear Rate (1/s)</th>
<th>Mean Wall Shear Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>35.89</td>
<td>0.09</td>
</tr>
<tr>
<td>20</td>
<td>68.98</td>
<td>0.147</td>
</tr>
</tbody>
</table>

The resulting shear stress values of 0.09 and 0.147 MPa are close to the critical wall shear stress values reported that are required to induce slip flow for polyethylene melts (0.1 to 0.3 MPa [57]). However, more data and a more detailed analysis of the flow in this type of cross section, similar to that of capillary or slit flow presented in
Section 2.4.2 should be done to characterize this particular polymer and its slip characteristics.

4.3.2 Color Change-Over Experiments

An initial evaluation of the in-line data indicated that an offset between the two days of experimentation was present. The following sections identify the cause of the observed offset and provide the methods that were used to successfully remove it. A detailed discussion of the in-line color change-over data is then presented.

4.3.2.1 Original In-Line Data

The factorial set of color change-over experiments were conducted over two days, with the duplicate set conducted on the second day. Examination of the L*a*b* color coordinates for the Blue to Purge change-over at 10 RPM, presented in Figures 4.15a to 4.15c, showed an offset in the L* color co-ordinate data between the two days but no corresponding offset in the a* and b* results. This offset was present in all of the remaining L* values. Since the calibration procedure was performed prior to both days of experimentation and yielded in-control results, an investigation into the offset of the L* values was conducted and is presented in the following section.

4.3.2.2 Application of the Spectral Correction Factor

Detailed analysis of the control chart calibrations showed that the reflectance curves from the second day were offset a constant percentage across the spectrum. The literature identified this as an error incurred while referencing the white reflectance
standard [30]. Visual inspection of the white standard showed that it had deteriorated over the two years of its use and imperfections in its surface were now present. Using a different part of the white standard's surface from day to day resulted in an offset in the white reference setting. This constant percentage offset effects only the $L^*$ color co-ordinate, which is a measure of the overall light intensity, and not the relative amount of light used to calculate the $a^*$ or $b^*$ color co-ordinates. Since the offset occurred in the calibration, it explains the offset seen in the remaining in-line $L^*$ values.

![Figure 4.15a: L* Blue to Purge Color Change-Over at 10 RPM](image)

![Figure 4.15b: a* Blue to Purge Color Change-Over at 10 RPM](image)

![Figure 4.15c: b* Blue to Purge Color Change-Over at 10 RPM](image)

Equation (14) in Section 2.2.2.4 was applied to correct the white referencing error present in the data. The first 10 scans of the day were used to calculate the correction.
factor. For industrial applications, using the first 10 scans allows for the offset in the spectral data to be both quickly identified and corrected, therefore allowing accurate monitoring over the subsequent production run. For each scan, the correction factor was determined by using the method of least squares.

The correction factors from Equation (14) used for the red/purge and blue/purge experiments are given in Table XII. Figure 4.16 shows the effect of applying the spectral correction factor to a reflectance curve from the Blue to Purge change-over at 10 RPM. The application of the correction factor increases the intensity of the reflectance curve across the spectrum without adversely effecting the shape of the curve, thereby removing the offset in the L* value without effecting either the a* or b* values.

<table>
<thead>
<tr>
<th>Color Change-Over Experiment</th>
<th>Spectral Correction Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red/Purge</td>
<td>9.51</td>
</tr>
<tr>
<td>Blue/Purge</td>
<td>8.41</td>
</tr>
</tbody>
</table>

Table XII: Spectral Correction Factors for Change-Over Experiments

Figure 4.16: Blue Color Chip Reflectance Curves showing Application of the Spectral Correction Factor
4.3.2.3 In-Line Color Change-Over Results

The effect of changing the variables "color change-over direction" (color to purge or purge to color) and "screw speed (RPM)" on changes in the L*a*b* color co-ordinates for both the red and blue experiments was investigated.

4.3.2.3.1 Red/Purge Change-Over Experiments

The in-line L*a*b* color co-ordinates as a function of time are presented in Figures 4.17a to 4.17c for the Red to Purge change-over. Each figure presents the duplicate runs conducted at both 10 and 20 RPM. The effect of increasing RPM is evident by observing the time required for the change-over to first become evident. This "time delay" was halved when the RPM was doubled for all three color co-ordinates. As anticipated, the time to reach the new steady state was also more rapid at the higher RPM setting.

Figure 4.17a shows the L* color co-ordinate increasing from the darker red color to the lighter off-white color exhibited by the purge compound. As more purge enters the system, an increase in the random noise occurs. A visual examination of the purge compound off-line shows that it is not homogenous in composition or color, and this effect is seen in the remaining in-line data.

Figure 4.17b shows the a* color co-ordinate first increasing and then decreasing to the final steady state as the red polymer is replaced by the purge compound. The temporary increase in the a* co-ordinate could be the effect of the purge compound displacing the red pigmentation from the interior of the extruder.
Figure 4.17a: L* Red to Purge Color Change-Over

Figure 4.17b: a* Red to Purge Color Change-Over

Figure 4.17c: b* Red to Purge Color Change-Over

Figure 4.18: Red Reflectance Curves Identifying Post Calibration Drift

Figure 4.17c shows the b* color co-ordinate for the red to purge change-over. The b* color co-ordinate remains constant, then decreases in value only to slowly increase again to its original steady state value. The initial and final values of the b* color co-ordinate has increased from the run conducted at 10 RPM to the run conducted at 20 RPM for both days of experimentation. Since the runs at the different RPM settings were conducted on the same day, this observation was further examined.

The color chips that were used in the control chart calibration methodology were scanned at the conclusion of each day of in-line testing. Figure 4.18 presents the reflectance curves obtained from the red color chip at the beginning and end of the in-line
experiments. The reflectance curve obtained at the end of the day is slightly lower in intensity but exhibits large differences in the low wavelength region (380nm to 500nm). This region represents the blue portion of the electromagnetic spectrum and the resulting decrease in reflection would be associated with an increase in the $b^*$ value (more yellow/less blue). The changes in the $L^*$ and $a^*$ color co-ordinates were less than five percent and therefore had minimal effect on the corresponding in-line data. Thus, a "within a day" calibration drift was apparently responsible for the changes in $b^*$. As it will be seen this phenomenon was observed again in a subsequent occasion indicating that additional calibrations during a day are sometimes necessary.

Figures 4.19a to 4.19c inclusive present the in-line $L^*a^*b^*$ color co-ordinates for the Purge to Red change-over at 10 and 20 RPM. The effect of color change-over direction is clearly seen in all three color co-ordinates as the time required to reach the new steady state values appears to be less than half the time required for the reverse (red to purge) color change-over at both RPM settings. The effect of increasing the RPM is again evident as the "time delay" was halved when the RPM was doubled for all three color co-ordinates.

![Figure 4.19a: $L^*$ Purge to Red Color Change-Over](image)

![Figure 4.19b: $a^*$ Purge to Red Color Change-Over](image)
Figure 4.19a shows the L* color co-ordinate change from the steady state value for the purge compound back to the steady state value of the red polymer. The inhomogeneous nature of the purge compound is again clearly seen as the noise decreases in the in-line data as red polymer is introduced back into the system. The in-line system is also sensitive to process upsets that can occur as evident in the L* curve for Day 2 at 10 RPM.

Figure 4.19b shows the a* color co-ordinate change from the purge to the red polymer. The transition occurs quite drastically over a few minutes, appears to peak and then decrease slightly to the steady state value. Figure 4.19c shows the b* color co-ordinate change from purge to red. The effect of post calibration drift is again evident as the b* value increases between the runs at 10 RPM and 20 RPM but also slightly within an individual run.

Off-line samples, obtained at the same time as the in-line monitoring was performed, qualitatively confirmed that the monitor was reporting accurate color changes.
However, radial non-uniformity of the color in these samples precluded accurate quantitative analysis.

4.3.2.3.2 Blue/Purge Change-Over Experiments

The in-line L*ab* color co-ordinates for the Blue to Purge change-over are presented in Figures 4.20a to 4.20c respectively, each showing the duplicate runs at both RPMs. Increasing the RPM had an identical effect as it did on the red/purge change-over, as the time delay before the color change-over is first evident was halved with doubling the RPM setting.

Figure 4.20a shows the change in the L* color co-ordinate as the color changes from blue to purge. In a similar manner to the red to purge change-over, the L* gradually changes from the darker blue to the lighter, off-white purge material. The noise present in the in-line data again increases as purge is introduced into the system with similar results present in the remaining blue/purge in-line data.

Figure 4.20b shows the change in the a* color co-ordinate from blue to purge. It is seen that the a* value actually decreases, before increasing to the steady state value of the purge material. This decrease in the a* color co-ordinate indicates that the sample is becoming more green in color before changing to the purge material, an observation that was verified by observing the off-line samples collected during this time interval.

Figure 4.20c shows the change in the b* color co-ordinate for the blue to purge change-over. The in-line data shows that the b* value decreases in magnitude, indicating that more blue is present during this portion of the change-over, a similar trend to that observed during the red to purge change-over. After the initial decrease in the b* color
Figure 4.20a: L* Blue to Purge Color Change-Over

Figure 4.20b: a* Blue to Purge Color Change-Over

Figure 4.20c: b* Blue to Purge Color Change-Over

Figure 4.21a: L* Purge to Blue Color Change-Over

Figure 4.21b: a* Purge to Blue Color Change-Over

Figure 4.21c: b* Purge to Blue Color Change-Over
co-ordinate, it increases to the steady state value of the purge material as no more blue pigment is present in the polymer.

The in-line L*a*b* color co-ordinates for the Purge to Blue color change-over are presented in Figures 4.21a to 4.21c respectively, each showing the duplicate runs at both RPMs. The effect of color change-over direction is evident as each color co-ordinate shows that the time required to complete the change-over process is well less than half the time required for the reverse (blue to purge) change-over at each RPM setting.

Figure 4.21a shows a more rapid change in the L* color co-ordinate as the blue replaces the purge compound in the extruder. Figure 4.21b shows the a* color co-ordinate decrease drastically, and then increase back to the final steady state value for the blue polymer. Figure 4.21c shows the b* color co-ordinate decreasing sharply, plateau for a small time interval and then decrease further to the final steady state value for the blue polymer. A closer investigation of Figure 4.20c and Figure 4.21c shows that the b* values for the runs conducted at 20 RPM are higher in magnitude than for the runs conducted at 10 RPM, again indicating the need for additional calibrations during the day.

![Figure 4.22: Blue Reflectance Curves Identifying Post Calibration Drift](image-url)

Figure 4.22: Blue Reflectance Curves Identifying Post Calibration Drift
Figure 4.22 shows the reflectance curves obtained from the blue color chip at the beginning and end of the day of in-line experimentation. The blue reflectance curve obtained after the completion of experimentation shows a decrease in intensity across the spectrum therefore confirming post calibration drift. Although the decrease in intensity was not as drastic as for the red/purge experiments, the resulting b* value increased in magnitude indicating more yellow (or less blue) was present and therefore explains the increase in the in-line b* values. The change in the L* and a* color co-ordinates was again less then five percent and therefore only minimally effected the in-line data.

4.3.2.3.3 Comparison between Red and Blue Change-Over Experiments

The time required for the change-over to first become evident was halved when the RPM was doubled for both color experiments, irrespective of the change-over direction. The direction of color change-over did have a significant effect on the time required to reach new steady state values and differences were observed between the colors. These differences indicated that pigment formulation also impacts the process of color change-over. The time required to reach a new steady state was much less for the blue pigmented LLDPE than it was for the red pigmented LLDPE at the same operating conditions for the purge to color change-over. Examination of the pigment formulation shows that the carrier resin for the blue pigment has a lower melt flow index than the red pigment, and therefore is more viscous than the red pigment formulation. The data also shows that the less viscous purge material required more time to displace both the red and blue colored LLDPE for the color to purge change-over. Finally, the need for re-calibration during the day was evident in two runs because of a drift in the value of b*.
4.3.3 Residence Time Distribution Analysis

Residence time theory provides a method that is used to assess the performance of a chemical reactor or system. The in-line reflectance data can be used to calculate the Cumulative, $F(t)$ and Washout, $W(t)$, residence time distributions. The RTDs are then used to calculate the mean residence time thereby allowing the normalization of the data to see if a universal RTD exists for the process of a color change-over in a single screw extruder.

4.3.3.1 Calculation of Residence Time Distributions

The model for calculating the RTDs presented in Appendix A. was used on the in-line data obtained during a color change-over run. Each change-over provides two RTDs, $W_1(t)$ tracks the component that is being removed from the system and $F_2(t)$ tracks the component that is being added to the system. It is noted that the sum of $W_1(t)$ and $F_2(t)$ does not necessarily equal unity during the transition because they are tracking different quantities. The separate RTDs track the amount of each component that is present in relation to their initial or final values.

Figure 4.23 shows the results obtained for the Red to Purge change-over at both RPM settings (day 1 data only). $W_1(t)$ (red) clearly starts at a value of unity and decreases to the expected value of zero, indicating that all of the red material has been removed. $F_2(t)$ (purge) starts at zero and increases up to the final value of unity, indicating that only purge is now present in the system. $F_2(t)$ at 20 RPM shows a negative deviation, but Section 4.3.3.2 will show that the error is no more than five percent.
Figure 4.23: Red to Purge RTDs

Figure 4.24: Purge to Red RTDs

Figure 4.24 presents the RTDs for the Purge to Red change-over (day 1 data only). $W_1(t)$ (now the purge compound) decreases from unity to zero as $F_2(t)$ (now the red LLDPE) increases from zero to unity, marking the end of the change-over.

The effect of increasing RPM on the RTDs is identical to its effect on the color co-ordinate curves. The time delay that is present before the change in concentration is first evident is halved when the RPM is doubled for both color directions. The direction of color change-over affects the time required to reach the new steady states but the results are consistent with the times required for the $L^*a^*b^*$ color co-ordinate curves at both RPM settings.

Figure 4.25: Purge to Red RTDs Both Days
Figure 4.25 presents the RTDs for the Purge to Red change-over for both days of experimentation. The strong degree of overlap between the days shows the repeatability of experiments conducted. The model is also sensitive to process upsets that occur as seen by the deviation occurring between the 12 to 15 minute mark of the run of the second day at 10 RPM. This same process upset was evident in the corresponding in-line L* color co-ordinate curve previously presented in Figure 4.19a.

Figures 4.26 and 4.27 present the RTDs for Blue to Purge and Purge to Blue respectively (day 1 data only). For both change-over directions it is clearly seen that the $W_1(t)$ value decreases from its initial value of unity to its final steady state value of zero, with the $F_2(t)$ value traversing in the reverse manner. The effect of doubling the RPM is identical to the red/purge RTDs as the value of the time delay is halved. The direction of color change-over affects the time required to reach the new steady states but are again roughly equivalent to the times required for the in-line L*a*b* color co-ordinate curves.

4.3.3.2 Calculation of Mean Residence Times

The mean residence times for the Cumulative and Washout residence time distributions were calculated using the techniques presented in Section 2.4.3. The mean
residence times for the Red to Purge and Purge to Red change-over experiments are presented in Tables XIII and XIV respectively.

Table XIII: Mean Residence Times for Red to Purge Change-Over

<table>
<thead>
<tr>
<th>RPM</th>
<th>Residence Time Distribution</th>
<th>( \bar{t} ) (min) Day 1</th>
<th>( \bar{t} ) (min) Day 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>( W_1(t) )</td>
<td>18.87</td>
<td>19.23</td>
</tr>
<tr>
<td>10</td>
<td>( F_2(t) )</td>
<td>23.42</td>
<td>24.57</td>
</tr>
<tr>
<td>20</td>
<td>( W_1(t) )</td>
<td>9.5</td>
<td>9.28</td>
</tr>
<tr>
<td>20</td>
<td>( F_2(t) )</td>
<td>12.88</td>
<td>12.63</td>
</tr>
</tbody>
</table>

Table XIV: Mean Residence Times for Purge to Red Change-Over

<table>
<thead>
<tr>
<th>RPM</th>
<th>Residence Time Distribution</th>
<th>( \bar{t} ) (min) Day 1</th>
<th>( \bar{t} ) (min) Day 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>( W_1(t) )</td>
<td>8.24</td>
<td>8.65</td>
</tr>
<tr>
<td>10</td>
<td>( F_2(t) )</td>
<td>10.15</td>
<td>11.18</td>
</tr>
<tr>
<td>20</td>
<td>( W_1(t) )</td>
<td>4.09</td>
<td>4.36</td>
</tr>
<tr>
<td>20</td>
<td>( F_2(t) )</td>
<td>5.49</td>
<td>5.44</td>
</tr>
</tbody>
</table>

Examination of the data shows that doubling the RPM reduces the mean residence time approximately in half for both color change-over directions, which is consistent with Equations (27) and (28). Comparison of the \( \bar{t} \) values shows that the component being removed, \( W_1(t) \), consistently has a slightly lower mean residence time than the component being added to the system, \( F_2(t) \). This result indicates that on average, component one is removed from the system before component two has completely entered the system. The mean residence time for the purge to red change-over is less than half the value for the red to purge change-over, clearly showing the effect of color change-over direction. These results confirm what was seen in both the in-line L*a*b* color co-ordinate curves and the concentration ratios previously presented.
As mentioned previously, the $F_2(t)$ curve for the change-over from red to purge at 20 RPM showed a minor negative deviation. If the curve was adjusted so that it was equal to the expected zero value for the duration of the deviation, the resulting mean residence time would be 12.45 minutes, a difference of less than four percent.

The calculation of mean residence times based on the $F_2(t)$ and $W_1(t)$ curves are sensitive to random fluctuations occurring in the data. The differences between the $\tilde{t}$ values calculated for Day 1 and Day 2 is attributed to the random noise present in Figures 4.23 to 4.27 inclusive. The mean residence times for the Blue to Purge and Purge to Blue change-over are given in Tables XV and XVI respectively.

### Table XV: Mean Residence Times for Blue to Purge Change-Over

<table>
<thead>
<tr>
<th>RPM</th>
<th>Residence Time Distribution</th>
<th>$\tilde{t}$ (min) Day 1</th>
<th>$\tilde{t}$ (min) Day 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$W_1(t)$</td>
<td>15.48</td>
<td>15.95</td>
</tr>
<tr>
<td>10</td>
<td>$F_2(t)$</td>
<td>17.51</td>
<td>18.71</td>
</tr>
<tr>
<td>20</td>
<td>$W_1(t)$</td>
<td>8.38</td>
<td>7.9</td>
</tr>
<tr>
<td>20</td>
<td>$F_2(t)$</td>
<td>9.81</td>
<td>8.93</td>
</tr>
</tbody>
</table>

### Table XVI: Mean Residence Times for Purge to Blue Change-Over

<table>
<thead>
<tr>
<th>RPM</th>
<th>Residence Time Distribution</th>
<th>$\tilde{t}$ (min) Day 1</th>
<th>$\tilde{t}$ (min) Day 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$W_1(t)$</td>
<td>5.83</td>
<td>5.76</td>
</tr>
<tr>
<td>10</td>
<td>$F_2(t)$</td>
<td>6.76</td>
<td>6.91</td>
</tr>
<tr>
<td>20</td>
<td>$W_1(t)$</td>
<td>3.38</td>
<td>3.22</td>
</tr>
<tr>
<td>20</td>
<td>$F_2(t)$</td>
<td>3.59</td>
<td>3.90</td>
</tr>
</tbody>
</table>

The calculated mean residence times show that increasing RPM decreases the mean residence time for both change-over directions. The mean residence time based on the $W_1(t)$ curve is again slightly less than the mean residence time based on the $F_2(t)$ curve, indicating that the component one is removed before component two has
completely entered the system. The difference in the calculated times from Day 1 and Day 2 is again attributed to the random noise/fluctuations occurring in the residence time distribution curves used in this analysis.

The direction of change-over shows a dramatic effect on the calculated mean residence times. The mean residence time for the direction of Purge to Blue is close to one third the value for the direction of Blue to Purge at both RPM settings. This effect is confirmed when cross-referenced to the in-line L* a* b* color co-ordinate curves and the residence time distributions previously presented (seen in examining the time scale). This differs from the value of one half that was observed in the mean residence time calculations for the Red/Purge change-over experiments. It is clear that the viscosity and pigmentation in the color formulations affect the time scale for the change-over process.

4.3.3.3 Normalization of RTD and Color Change-Over Curves

Theory introduced in Section 2.4.3 stated that for a single screw extruder a universal residence time distribution could be generated by plotting the RTDs as a function of $t/\bar{t}$ where $\bar{t}$ is the mean residence time for the respective RTD curve [56].

Figures 4.28 and 4.29 present the normalized RTDs for the Red to Purge and Purge to Red change-over experiments respectively. Figures 4.30 and 4.31 present the normalized RTDs for the Blue to Purge and Purge to Blue change-over experiments respectively. Each figure shows the RTDs obtained using only the data from the first day of experimentation.
Each figure clearly shows how the RTD curves at 20 RPM overlap significantly the RTD curves at 10 RPM. The same degree of overlap was obtained for the duplicate runs and similar curves were obtained if all of the data was plotted on one graph. These figures show that the process of color change-over, for a particular condition (ie. red to purge), is "universal" and that the RPM only effects the time scale without altering its shape. The factors that effect the shape of the RTD curve are the "direction of color change-over" and the "pigmentation" (and hence viscosity) of the colors used.
The mean residence time was also used to normalize the \( L^*a^*b^* \) color co-ordinate curves. The average of the mean residence times, \( W_1(t) \) and \( F_2(t) \), for a particular change-over run was used to normalize the color curves since each color change-over provides two different RTD functions. The results for the Blue to Purge change-over are shown in Figures 4.32a to 4.32c inclusive.

![Figure 4.32a: Normalized \( L^* \) Blue to Purge Color Change-Over](image)

![Figure 4.32b: Normalized \( a^* \) Blue to Purge Color Change-Over](image)

![Figure 4.32c: Normalized \( b^* \) Blue to Purge Color Change-Over](image)

The overlap in these figures clearly show that the color co-ordinate curves are not different in shape but only in the time scale for which they span for the two RPM settings. Therefore, the \( L^*a^*b^* \) color co-ordinate curves determined here were also "universal" in nature in that their shape is effected by the color change-over direction and
pigmentation and not by the RPM setting. Similar results were obtained for all color coordinate curves, for each color change-over direction and color (blue or red).

4.3.3.4 Mixing, Flow and Adhesion Effects

The RTD curves of the concentration ratios do not match perfectly the theoretical one presented for a single screw extruder. Since the concentration profiles were calculated based on the material a depth $\delta$ into the flow, we are primarily seeing the material close to the extruder walls and sapphire window. Therefore, the effect of the colored materials adhering to the interior surfaces and the phenomenon of stick-slip flow will be reflected in these RTD curves. The RTD curves do show the characteristic time delay before the concentration begins to change. The rate at which a material is stripped from the interior of the extruder has been seen already in the RTD curves for the differences in color and direction. The possible adhesion of material also reflects the shape in which the actual $L^*a^*b^*$ color co-ordinate curves may change as one pigment in the formulation may be removed preferentially over others. This further indicates that the pigmentation formulation and its resulting viscosity are primary factors in the process of color change-over.
5.0 CONCLUSIONS

i. An initial assessment of the new charge coupled device (CCD) spectrometer for in-line monitoring revealed that reliable data was not being obtained and sensitivity of the instrument to color changes was in question. Development of a new operating procedure was identified as the possible solution to the problem.

ii. An operating procedure was developed and the CCD spectrometer was then successfully used to monitor the color of pigmented polymers in-line during the extrusion process. The statistically based procedure utilizes control charts and, when necessary, spectral correction factors.

iii. The sensitivity of the instrument was demonstrated. It was shown that statistical hypothesis testing could be used to specify the number of replicates necessary for even very similar colors to be distinguished.

iv. A method of extracting concentration ratios from the reflectance spectra provided residence time distributions and washout functions to be derived from the color changeover data. Superposition of the distributions at the two different screw RPMs using the mean residence time to define a dimensionless time was obtained and is in accord with what was expected from theoretical residence time distribution theory.

v. Utilizing the newly developed operating procedure, the effect of extruder screw RPM on color change-overs were examined. For the two screw RPM's investigated
the shape of L*a*b* curves and the shape of residence time distributions were unchanged by the RPM setting. Use of dimensionless time was shown to permit "universal" curves of the color co-ordinates versus time as well as the residence time distributions so that the effect at RPM's not investigated experimentally can be predicted.

vi. Shear stress at the wall of the monitor interface window was estimated and found to be in the range where slip at the wall may occur.
6.0 RECOMMENDATIONS

i. The possibility of increasing monitor performance by scheduling additional calibrations during a run should be examined. Within run calibration drift was sometimes observed in this work.

ii. The color chips currently used in the control chart methodology need to be replaced with ones that are more stable with time. Although these chips are available, they too need to be replaced before their respective “shelf lives” are reached. This applies to the white standard used in the methodology as well.

iii. The use of a sapphire window in the off-line calibration procedure will help reduce the variability of the system when monitoring in-line. Incorporating its effect will help differentiate errors that are due to extruder effects, calibration effects or those due to the sapphire window itself.

iv. A more detailed investigation into the slip flow characteristics of the carrier resin (Dowlex 2045) is required to confirm the occurrence of slip flow and the required wall shear stress to initiate it. The effect that the color pigments (and purge compound) used in this study have on the slip flow characteristics should also be investigated.
v. Treating the surface of the sapphire window with a fluoropolymer may improve the response of the in-line color monitoring system. The surface treatments may promote slip flow to occur at the window surface thereby decreasing monitor response time.
REFERENCES


5. ASTM E 308-94. Standard Practice for Computing the Colors of Objects by Using the CIE System. 744-773


41. Ocean Optics Inc. Home Page (www.oceanoptics.com)


44. Pantone Color Formula Guide. 14th Printing, 1999


APPENDIX A:
ABSORPTION MODEL FOR RESIDENCE TIME DISTRIBUTIONS

Absorption Equation

As mentioned in Section 2.1.7 an absorption model based on the Beer-Lambert law can be used to calculate concentration profiles of the pigmented polymer during a color change-over experiment. The absorbance is given by:

\[ A(\lambda) = a(\lambda) \delta C \]  \hspace{1cm} \text{(A-1)}

where:

- \( A(\lambda) \) = absorbance, dependent on wavelength and concentration \([\text{absorbance units}]\)
- \( a(\lambda) \) = an absorption coefficient dependent on wavelength and concentration \([\text{L/mol*cm}]\)
- \( \delta \) = a penetration depth into the polymer substrate, similar to the path length (b) in the Beer-Lambert law \([\text{cm}]\)
- \( C \) = concentration of the pigment in the polymer substrate \([\text{mol/L}]\)

Model Assumptions

1) the penetration depth is constant for all pigments (blue, red and purge)
2) negligible scatter of light
Concentration Profiles and Residence Time Distributions

During a color change-over experiment, as the two pigments mix, the absorbance at any time at a specific wavelength, \( A_t(\lambda) \), is equal to the additive result of the two species present.

\[
A_t(\lambda) = a_1(\lambda) \cdot C_1 + a_2(\lambda) \cdot C_2 \quad (A-2)
\]

When two different wavelengths are used we then have two equations and two unknowns for which the quantities of the absorption coefficients and penetration depth, \( a_1(\lambda)\delta \) for component 1 and \( a_2(\lambda)\delta \) for component 2, need to be solved. At \( t = 0 \), only component 1 is present \((C_1 = C_{1,t=0} \text{ and } C_2 = 0)\), allowing the determination of \( a_1(\lambda_1)\delta \) in Equation (A-3) and \( a_1(\lambda_2)\delta \) in Equation (A-4):

\[
A(\lambda_1)_{t=0} = a_1(\lambda_1) \cdot C_{1,t=0} \quad \text{or} \quad a_1(\lambda_1)\delta = \frac{A(\lambda_1)_{t=0}}{C_{1,t=0}} \quad (A-3)
\]

\[
A(\lambda_2)_{t=0} = a_1(\lambda_2) \cdot C_{1,t=0} \quad \text{or} \quad a_1(\lambda_2)\delta = \frac{A(\lambda_2)_{t=0}}{C_{1,t=0}} \quad (A-4)
\]

At \( t = \infty \) only component 2 is present \((C_1 = 0 \text{ and } C_2 = C_{2,t=\infty})\) allowing the determination of \( a_2(\lambda_1)\delta \) in Equation (A-5) and \( a_2(\lambda_2)\delta \) in Equation (A-6):

\[
A(\lambda_1)_{t=\infty} = a_2(\lambda_1) \cdot C_{2,t=\infty} \quad \text{or} \quad a_2(\lambda_1)\delta = \frac{A(\lambda_1)_{t=\infty}}{C_{2,t=\infty}} \quad (A-5)
\]
\[ A(\lambda_2)_{t_{\infty}} = a_2(\lambda_2) \delta C_{2,t_{\infty}} \quad \text{or} \quad a_2(\lambda_2) \delta = \frac{A(\lambda_2)_{t_{\infty}}}{C_{2,t_{\infty}}} \quad (A-6) \]

Equation (A-2) can now be written for both wavelengths at any time yielding the required two equations and two unknowns:

\[
A(\lambda_1)_t = A(\lambda_1)_{t=0} \frac{C_{1,t=0}}{C_{1,t=0}} + A(\lambda_1)_{t_{\infty}} \frac{C_{2,t_{\infty}}}{C_{2,t_{\infty}}} \quad (A-7)
\]

\[
A(\lambda_2)_t = A(\lambda_2)_{t=0} \frac{C_{1,t=0}}{C_{1,t=0}} + A(\lambda_2)_{t_{\infty}} \frac{C_{2,t_{\infty}}}{C_{2,t_{\infty}}} \quad (A-8)
\]

The above equations can be simplified by substituting
\[ W_1(t) = \frac{C_{1,t=0}}{C_{1,t=0}} \quad \text{and} \quad F_2(t) = \frac{C_{2,t_{\infty}}}{C_{2,t_{\infty}}}, \]
where \( W_1(t) \) is the Washout residence time distribution based on component 1 and \( F_2(t) \) is the Cumulative residence time distribution based on component 2.

\[
A(\lambda_1)_t = A(\lambda_1)_{t=0} W_1(t) + A(\lambda_1)_{t_{\infty}} F_2(t) \quad (A-9)
\]

\[
A(\lambda_2)_t = A(\lambda_2)_{t=0} W_1(t) + A(\lambda_2)_{t_{\infty}} F_2(t) \quad (A-10)
\]
Equations A-9 and A-10 can be used to calculate the residence time distributions of each component as a function of time over the duration of a color change-over experiment. Previous experimental work [25] has shown that the use of only a single wavelength for each equation can result in a large degree of noise being present in the calculated RTDs. It is known that in spectrometric analysis, the more wavelengths that are used the lower the level of noise in the resulting data is. The governing equations can be modified by using an integrated absorbance (calculating the area under the curve) for a given wavelength range. This modification was designed to help reduce the amount of noise previously encountered. The modified equations are with wavelength ranges ($\lambda_1$ to $\lambda_2$) and ($\lambda_3$ to $\lambda_4$):

\begin{equation}
\int_{\lambda_1}^{\lambda_2} A_{\lambda} d\lambda = W_1(t) \int_{\lambda_1}^{\lambda_2} A_{\lambda=0} d\lambda + F_1(t) \int_{\lambda_1}^{\lambda_2} A_{\lambda=x} d\lambda
\end{equation}

(A-11)

\begin{equation}
\int_{\lambda_3}^{\lambda_4} A_{\lambda} d\lambda = W_2(t) \int_{\lambda_3}^{\lambda_4} A_{\lambda=0} d\lambda + F_2(t) \int_{\lambda_3}^{\lambda_4} A_{\lambda=x} d\lambda
\end{equation}

(A-12)

The above model is the general form and the integrals are calculated using the trapezoidal approximation. The above model can now be used for either a wavelength range or for individual wavelengths.

For solving the system of equations, the wavelengths are chosen by examining the absorbance curves of each individual species (again, for a color change-over experiment
these are represented by time = 0 and time = ∞, the two steady states of the experiment) which is discussed in the following section.

**Wavelength Selection**

The steady state absorbance curves for the blue/purge change-over and red/purge change-over are shown in Figures A-1 and A-2 respectively. The best wavelength regions to use in the analysis are the ones in which a) the errors in the absorbance are at a minimum and b) the individual spectra are as different in shape as possible [28]. Figures A-1 and A-2 clearly show the difficulties in choosing the best wavelength regions. The absorbance curve of the purge compound has a very high reflectance due to its off-white color. This results in very low absorbance values across the spectrum from roughly 500nm to 780nm restricting the selection of wavelengths for this compound to the region before 500nm. Being restricted to this region is not really the preferred situation as a local absorbance maximum would provide the best precision. Secondly, the absorbance curves of both the blue and red polymer are almost constant over large wavelength regions. This does allow the use of a larger wavelength region but since we are restricted to a small region for the purge absorbance curve, an equivalent small range was selected for each color. Due to the shape of the steady state absorbance curves, it was decided that a 5nm wavelength range was best suited for the analysis. The wavelength regions chosen were: red: 500nm to 505nm, blue: 750nm to 755nm and purge: 400nm to 405nm. These small identical increments meant that when we use Equations A-11 and A-12 with the trapezoidal rule, we are effectively using the average absorbance over each wavelength range and Equations A-9 and A-10.
The results presented using this analysis are given in Section 4.3.3.1 and are of much better quality then the ones calculated using a similar analysis in the previous work by C.Gilmor [25]. It is clear that the use of the operating procedure for in-line monitoring has helped improve the quality of the data used for this analysis.

In conclusion, the model was presented in the general form so to be applicable to situations in which the absorbance curves of the two steady state species differ more than the ones obtained here. The decision to not use area under the spectra is a consequence of the pure component absorbance curves for the materials used.

![Figure A-1: Steady State Blue/Purge Absorbance Curves](image1)

![Figure A-2: Steady State Red/Purge Absorbance Curves](image2)
APPENDIX B:
COLOR MONITORING PROBE DESIGNS

Discussions with Colortech Inc. revealed that the melt-at-die interface currently used in laboratory work was not as desirable in a manufacturing environment. A probe that could be rapidly inserted into pre-existing holes in the extruder was requested.

Most extruders are all-ready equipped with multiple holes for Dynisco pressure transducers, the industrial standard. A probe that fits into a Dynisco pressure transducer can be immediately inserted into most industrial extruders allowing anyone to conduct in-line color monitoring without irreversible modifying their equipment (i.e. by adding a transition piece, or by drilling into the die or barrel of the extruder).

Two designs for dedicated color monitoring probes have been developed. The first design uses an outer shell that contains the sapphire window and allows the reflection probe from Ocean Optics Inc. to be readily inserted. The second design incorporates the sapphire window and reflection probe into one complete unit. Each design is described accordingly, however neither has been tested experimentally.

**Design I: University of Toronto Color Probe**

Aspects from the multi-functional interface designs were incorporated into the design of this color probe. The probe makes use of an inner and outer shell, the sapphire window and the copper gasket. The outer shell, shown in Figure B-1, has the dimensions of the standard Dynisco pressure transducer and is constructed from stainless steel. The only variable that needs to be adjusted is the absolute length of the probe so it can fit in extruders of varying wall thickness.
The outer shell has a 25.4 mm HEX head with the inner portion threaded to allow the inner shell to screw into place after the window and gasket are installed. A magnified view of the probe tip with the relevant design dimensions is given in Figure B-2.
probe tip required a change in the standard window dimensions. The thickness of the window was kept constant so to not change the associated optical properties. In order to fit the small dimensions (diameter) the window is to be made with a 60-degree angle instead of the 45-degree angle previously used in the interface design. The sapphire window is designed to protrude 0.5mm into the flow, similar to the multi-functional interface designs. The new sapphire window and its dimensions are given in Figure B-3.

![Diagram of probe tip dimensions](image)

**Figure B-2: Magnified view of Outer Shell Probe Tip**
*(All dimensions in millimeters)*

A copper gasket is still used in the sealing process. The copper gasket was kept to the same thickness and only its diameter was changed. The copper gasket is given in Figure B-4.
The sapphire window and copper gasket are placed within the outer shell and the inner shell, shown in Figure B-5, is then inserted. The inner shell is also constructed from stainless steel. The inner and outer shells are fastened together at the top of the assembly (as indicated by the threads at the top of each piece) and the torque is transferred down the length of the shaft to the window and gasket to form the seal. The inner shell has an interior shaft 3.18mm in diameter. The fiber optic reflection probe from Ocean Optics is inserted into this space until it is flush with the top of the window. A setscrew located in the head of the inner shell is used to secure the position of the reflection probe so that it does not move due to extruder vibrations.
This is a special order probe as the standard outer diameter is 6.35mm. The cost for the smaller diameter probe is $850 (US), roughly $150 more than the standard probe. A major drawback is that they are made-to-order and are therefore not off the shelf items.

Figure B-5: Inner Shell of Color Probe Assembly
(All dimensions in millimeters)
This design allows anyone with a standardized Dynisco pressure transducer to conduct color monitoring. It makes use of only one reflection probe that can be removed when not in use. A plug would then be inserted to prevent dirt and dust from covering the surface of the window. If the sapphire window is damaged, spare assemblies of the probe housing can be pre-made and be in-stock items of the company. If a replacement is necessary, the reflection probe is removed, the damaged housing is removed from the extruder and a new housing screwed into the Dynisco pressure hole. The reflection probe can then be re-inserted and color monitoring can be re-initiated.

**Design II: University of Toronto/Ocean Optics Dedicated Color Probe**

This design was done in collaboration with Ocean Optics Inc. (Dunedin, FL) and removes the use of the two thin-walled shells described in the previous design. The sapphire window is incorporated into the actual stainless steel ferrule (probe tip) housing of the reflection probe built by Ocean Optics. The ferrule is also constructed with the dimensions of the standard Dynisco pressure transducer. The sapphire window is again designed to protrude 0.5mm into the polymer flow. The probe is presented in Figure B-6 and it shows the fiber optic bundle exiting the probe at the top of the probe which transmits the signal to and from the spectrometer.

The estimated cost was $1300 (US) at the time of the inquiry. While eliminating the number of parts and simplifying the installation of the color probe it increases the cost of replacement. If the current probe is damaged, a new one needs to be purchased at the above price. This system is also dedicated to color only as the previous design could allow other monitoring probes of 3.18mm diameter to be used.
Figure B-6: University of Toronto/Ocean Optics Inc. Dedicated Color Probe
(All dimensions in millimeters)
APPENDIX C: EXTRUDER DIMENSIONS AND NOMENCLATURE

Extruder Dimensions

The extrusion equations presented in Section 2.4.1 make use of generalized extruder nomenclature. The generalized diagram of a single screw extruder is given below in Figure C-1.

Where:

\[ D = \text{diameter of the barrel [cm]} \]

\[ H = \text{distance between the screw and the barrel [cm]} \]

\[ W = \text{distance between the screw flights [cm]} \]

\[ \theta = \text{the helix angle, the angle between the screw and the flight [radians]} \]

\[ l = \text{the length of the screw [cm]} \]

\[ z = \text{the unrolled channel length} = \frac{l}{\sin \theta} \text{ [cm]} \]
Equation (19) represented the total flow rate of polymer through a single screw extruder with a cylindrical die hole. For this equation, the following dimensions and variables are defined:

\[ N = \text{rotational frequency of the screw [RPM or s}^{-1}] \]
\[ R = \text{radius of cylindrical die [cm]} \]
\[ L = \text{length of cylindrical die [cm]} \]

Equations (27) and (28) represent the equations for calculating the Cumulative Residence Time Distribution for a single screw extruder. For these equations the following additional dimensions and variables are defined:

\[ y = \text{rectangular co-ordinate in the channel depth direction [cm]} \]
\[ V_b = \text{tangential velocity of the barrel surface relative to the screw [cm/s]} \]
\[ V_b = \pi N D \]
\[ Q_p = \text{volumetric pressure flow [cm}^3/\text{s]} \]
\[ Q_p = -\frac{P W H^3}{12 \eta^2} \]
\[ Q_d = \text{volumetric drag flow [cm}^3/\text{s]} \]
\[ Q_d = \frac{1}{2} \pi N D H W \cos \theta \]
\[ P = \text{pressure [Pa]} \]
\[ \eta = \text{viscosity of polymer melt [Pa s]} \]
APPENDIX D: PRECISION AND STATISTICAL MEASURES

Statistical Measures

An overview of the statistical measures used in the data analysis throughout this thesis is presented in this section. The normal calculation of a sample mean ($\bar{x}$) and standard deviation ($s$) of a data set are given as [21]:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n} \quad \text{(D-1)}$$

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \quad \text{(D-2)}$$

An alternative way of calculating the standard deviation is by the process of successive differences [37]. The formula for this measure is:

$$s = \sqrt{\frac{\sum_{i=1}^{n-1} (x_{i+1} - x_i)^2}{2(n-1)}} \quad \text{(D-3)}$$

The calculation of the standard deviation by the normal method is much more sensitive to any departures from flatness (such as a linear tilt or a parabolic curve) in the data. Therefore the method of successive differences allows an estimation of the random noise present in the data which may exhibit any of the above noted characteristics [37].

The coefficient of variation is a dimensionless quantity that measures the amount of variability in the data relative to the mean value. The coefficient of variation (c.v.) for a particular data set is calculated as [21]:

$$\text{C.V.} = \frac{s}{\bar{x}} \cdot 100\%$$
The calculation of 'residuals' for a data set can also be calculated by the method of successive differences. The formula for the computation of a residual is [37]:

$$\text{residual} = x_{i+1} - x_i$$  \hspace{1cm} (D-5)

Confidence Intervals

Confidence intervals are a measure of the precision in a parameter's true value. Their calculation is based on the assumption that the population distribution is normal. Confidence intervals based on the true population mean ($\mu$) is given by [21]:

$$\left( \bar{x} - z_{\alpha/2} \frac{\sigma}{\sqrt{n}} \right) < \mu < \left( \bar{x} + z_{\alpha/2} \frac{\sigma}{\sqrt{n}} \right)$$  \hspace{1cm} (D-6)

Where $\bar{x}$ is the sample mean and $\sigma$ is the population standard deviation. The level of confidence determines the value of $z_{\alpha/2}$ obtained from the 'Normal Distribution' ($\alpha = 1 - \text{ confidence level}$). If the standard deviation of the population is unknown and the sample size is large ($n>30$) then the sample standard deviation ($s$) can replace the population value ($\sigma$) in Equation D-5. If the sample size is small and the sample standard deviation is used the confidence limits become [21]:

$$c.v. = \frac{s}{x}$$  \hspace{1cm} (D-4)
The level of confidence determines the value of \( t_a \) which is obtained from the ‘t Distribution’ with \( \alpha \) calculated the same way as for the normal distribution. The value of \( v \) is the number of degrees of freedom calculated as: \( v = n-1 \).

A confidence interval can be calculated for standard deviations as well. These too make the assumption that the underlying population is normal and make use of the \( \chi^2 \) distribution. The confidence interval for a standard deviation is calculated as [21]:

\[
\left( \frac{\sqrt{n-1}s^2}{\chi_{ \frac{1}{2} n-1}^2} \right) \leq \sigma \leq \left( \frac{\sqrt{n-1}s^2}{\chi_{1-\alpha \frac{1}{2} n-1}^2} \right)
\]  

(D-8)

where the degrees of freedom is equal to \( n-1 \) and \( \alpha \) is equal to 1 - level of confidence.

**Hypothesis Testing**

Hypothesis Testing is often used to make an inference or a claim about the value of a population characteristic. It is also used to make an inference based on two samples to determine if the values are equivalent or different at a particular level of significance. For the hypothesis test on the difference between two population means for a two-tailed test, the following are defined [21].

\[
\left( \bar{x} - t_a \frac{s}{\sqrt{n}} \right) < \mu < \left( \bar{x} + t_a \frac{s}{\sqrt{n}} \right)
\]  

(D-7)
Null Hypothesis: \( \mu_1 - \mu_2 = \Delta_0 \) \hspace{1cm} (D-9)

Alternate Hypothesis: \( \mu_1 - \mu_2 \neq \Delta_0 \) \hspace{1cm} (D-10)

Test Statistic:
\[
z = \frac{\bar{x} - \bar{y} - \Delta_0}{\sqrt{\frac{\sigma_1^2}{m} + \frac{\sigma_2^2}{n}}} \hspace{1cm} (D-11)
\]

Here \( \bar{x} \) and \( \bar{y} \) are the respective sample means. \( \sigma_1 \) and \( \sigma_2 \) are the respective population standard deviations and \( m \) and \( n \) are the sample sizes for sample 1 and sample 2 respectively. The value of \( \Delta_0 \) and the confidence level to conduct the test are chosen a priori to the calculation of the test statistic. If the sample sizes are large (\( m>30, \; n>30 \)) then the sample standard deviation (s) can replace the population standard deviation (\( \sigma \)).

Once the test statistic has been calculated it is compared to the critical value determined by the normal distribution at the desired confidence level (\( z_{\alpha/2} \)). The Null Hypothesis is rejected and Alternative Hypothesis accepted if [21]:

\[
z \geq z_{\alpha/2} \hspace{1cm} \text{or} \hspace{1cm} z \leq -z_{\alpha/2} \hspace{1cm} (D-12)
\]
Determination of Minimum Sample Size

Sample sizes m and n can be determined considering both Type I and Type II Errors. A Type I error ($\alpha$) is incurred when the Null Hypothesis is rejected when in actuality it is true. A Type II ($\beta$) error is incurred when the Null Hypothesis is not rejected when in actuality it is false. If the two sample sizes are the same, the equation for the minimum number of samples for a two-tailed test is [21]:

\[
m = n = \frac{(s_i^2 + s_j^2)(z_{\alpha/2} + z_{\beta})^2}{(\Delta - \Delta_0)^2}
\]  

(D-13)
APPENDIX E: OPERATING PROCEDURE FOR COLOR MONITORING SYSTEM

The results from the off-line test methods to generate an accurate operating procedure for the color monitoring system are summarized below.

Warm Up Time: A five-hour warm-up time for the light source (LS1) was determined necessary from the drift evaluation experiments conducted. This warm-up time greatly exceeds the manufacturer's recommendation of 30 minutes.

Accurate Placement of Fiber Optic Probe: The reproducibility of the measurements and the generation of the control charts required that the same spot of the color chips be monitored. For this purpose a "color chip holder" was constructed to allow consistent alignment of the probe and the color chip. This procedure also required the color probe to be consistently aligned within the probe holder. This was accomplished by marking both the probe and the probe holder for future measurements.

Signal Averaging: The reduction of noise within a set of measurements was accomplished by averaging 20 instantaneous reflectance spectra per scan for both in-line and off-line measurements. This set point was determined the best for its reduction in the standard deviations of the L*a*b* color co-ordinate values, the quality of the reflectance curves obtained and the rate at which the system could acquire the scan (less than two seconds).
Control Charts: Control charts were generated as they provided a method to track the validity of the calibrations of the color monitoring system that were performed on a daily basis. They can also be used as an off-line test method to assess whether post calibration drift is occurring within the monitoring system.

Spectral Correction Factors: The spectral correction factors given in Equations (13) and (14) can be used to remove any errors that may occur in the photometric scale (reflectance value) when calibrating the monitoring system. These correction factors correct for errors in the black (0%) or white (100%) reference settings. Other correction factors are available in the published literature but were not required in this work.

Sensitivity: The developed operating procedure allows for the color monitoring system to discern small color differences off-line by using the previously mentioned conditions. This test procedure can employ statistical hypothesis testing of the data.

Operating Instructions: Operating instructions detailing the equipment set-up, software set-up, calibration verifications and the correct methods for conducting both off-line and in-line tests (incorporating the operating conditions specified by this procedure) have been prepared and are available to the user when needed.