Final Technical Report - Advanced Optical Sensors to Minimize Energy Consumption in Polymer Extrusion Processes

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Executive Summary

Project Objective: The objectives of this study are to develop an accurate and stable on-line sensor system to monitor color and composition on-line in polymer melts, to develop a scheme for using the output to control extruders to eliminate the energy, material and operational costs of off-specification product, and to combine or eliminate some extrusion processes.

Background: Polymer extrusion processes are difficult to control because the quality achieved in the final product is complexly affected by the properties of the extruder screw, speed of extrusion, temperature, polymer composition, strength and dispersion properties of additives, and feeder system properties. Extruder systems are engineered to be highly reproducible so that when the correct settings to produce a particular product are found, that product can be reliably produced time after time. However market conditions often require changes in the final product, different products or grades may be processed in the same equipment, and feed materials vary from lot to lot. All of these changes require empirical adjustment of extruder settings to produce a product meeting specifications.

Optical sensor systems that can continuously monitor the composition and color of the extruded polymer could detect process upsets, drift, blending oscillations, and changes in dispersion of additives. Development of an effective control algorithm using the output of the monitor would enable rapid corrections for changes in materials and operating conditions, thereby eliminating most of the scrap and recycle of current processing. This information could be used to identify extruder systems issues, diagnose problem sources, and suggest corrective actions in real-time to help keep extruder system settings within the optimum control region. Using these advanced optical sensor systems would give extruder operators real-time feedback from their process. They could reduce the amount of off-spec product produced and significantly reduce energy consumption. Also, because blending and dispersion of additives and components in the final product could be continuously verified, we believe that, in many cases, intermediate compounding steps could be eliminated (saving even more time and energy.).

Sensor design and development: The sensor system design consists of an optical probe and spectrometer that are connected via fiber optics. The probe operates while inserted directly in the process being measured. A color measurement via diffuse reflectance was selected as the method of choice. Two separate diffuse reflectance probe designs were pursued, one with 19 illuminating fiber optics and one pick up fiber, and a second with 7 illuminating fiber optics and one pick up fiber. Each design has the potential to provide the correct measurement, with different advantages in each case. Ultimately, trials in the extruder were conducted with the probe containing 7 illuminating fibers.

Lab and extruder testing: Laboratory testing of the probes initially showed that stray light was larger than desired. Mechanisms for correcting this were outlined and implemented. Successful color calibration methodology was implemented in the analyzer software. This calibration made use of calibrated external reflectance standards. Long term measurement trials illustrated system stability that was sufficient for making useful extruder measurements. On line trials of the probe and measurement system were conducted with a laboratory extruder. The goals of the onsite measurement trials were to evaluate the probe measurement capabilities and mechanical robustness in a polymer extruder at temperatures up to 300 °C and pressures up to 2000 psi. The optical measurements were made using a Guided Wave Model 508 UV/Vis diode array spectrometer system. Measurement over different levels of opacity showed the capability to measure color at

higher opacity materials, but some difficulty with translucent materials. Mechanical issues with fiber optic attachment methods caused an optical failure in the end.

Next steps: A revision of the fiber optic attachment mechanism has been proposed. Next steps will involve reliability testing of the attachment. Further testing on probe window brazing strength at different temperatures is also proposed.

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1. Introduction

According to a 2003 DOE Report, polymer production is responsible for 6% of industrial power consumption in the United States, and between 5% to 10% of that production requires tight color and composition control. We estimate that many of the polymer production processes requiring tight color and composition control could reduce their energy usage by more than 25% by using advanced optical sensors to continuously control extruder output. Typically off-spec product is recycled back through the process so that little material is wasted; however energy and processing time are lost. Estimates of the size of the internal recycle loop range from 5% to over 40%. Also, several extrusion processes are often involved in producing a plastic part. Some of these extrusion processes could be combined or eliminated by better control of mixing and dispersion of polymer components. The objectives of this study are to develop an accurate and stable on-line sensor system to monitor color and composition on-line in polymer melts, to develop a scheme for using the output to control extruders to eliminate the energy, material and operational costs of off-specification product, and to combine or eliminate some extrusion processes.

Guided Wave produces a line of advanced optical sensors to control color and composition in manufacture of consumer products like liquid detergents, pharmaceuticals and beverages. This sensor system could be further developed for application to the control of polymer extrusion processes. Polymer extrusion processes are difficult to control because the quality achieved in the final product is complexly affected by the properties of the extruder screw, speed of extrusion, temperature, polymer composition, strength and dispersion properties of additives, and feeder system properties. Extruder systems are engineered to be highly reproducible so that when the correct settings to produce a particular product are found, that product can be reliably produced time after time. However market conditions often require changes in the final product, different products or grades may be processed in the same equipment, and feed materials vary from lot to lot. All of these changes require empirical adjustment of extruder settings to produce a product meeting specifications. Optical sensors that can continuously monitor the composition and color of the extruded polymer could detect process upsets, drift, blending oscillations, and changes in dispersion of additives. Development of an effective control algorithm using the output of the monitor would enable rapid corrections for changes in materials and operating conditions, thereby eliminating most of the scrap and recycle of current processing. This information could be used to identify extruder systems issues, diagnose problem sources, and suggest corrective actions in real-time to help keep extruder system settings within the optimum control region.

Using these advanced optical sensors would give extruder operators real-time feedback from their process. They could reduce the amount of off-spec product produced and significantly reduce energy consumption. Also, because blending and dispersion of additives and components in the final product could be continuously verified, we believe that, in many cases, intermediate compounding steps could be eliminated saving even more time and energy.

One goal of this project is to demonstrate methods that can be used to control polymer extrusion processes with the effects of significantly reducing in-process scrap recycle and combining or eliminating extrusion operations. The 2003 DOE report, “U.S. Plastics Manufacturers Stand to Save Energy, Boost Competitiveness, and Reduce Costs”, states: “The plastics industry consumes

approximately 6% of all the energy used by U.S. industries, and it is valued at $6 billion (based on 1998 DOE and other data). DOE estimates that reducing the plastics industry's energy use by even 1% by 2010 could shave at least $100 million from its total annual energy costs."

This report also shows that energy savings of up to 10% could be achieved by following industrial 'best practices'. Larger energy reductions will require more fundamental changes in polymer manufacturing methods.

Polymer extrusion is an energy intensive process widely used throughout the plastics industry to mix additives and polymer compounds. Adequate dispersion of additives in polymers is essential to the performance and appearance of the final product. Colorants are some of the most common and important additives used in the polymer industry. Typically, additives are blended with polymer resins in a feed system and delivered to the extruder in small batches. The various components of the feed are heated and blended in the extruder to produce a molten uniform compound that can be molded into a useful shape, or chopped into pellets to be used in other extrusion operations. Often, there are three extrusion steps involved in the manufacture of a plastic part: master-batching, compounding, and molding. A master-batch operation involves blending raw materials with a low viscosity, easy to process polymer in order to uniformly disperse the raw materials at high concentration. The product of a master-batch operation is easy to handle pellets with well-dispersed additives at known concentrations. The purpose of a compounding operation is to blend master-batch additives and other components with polymers to formulate the polymer compound that will be used to mold or form the final product. The product of a compounding operation is easy to handle pellets with uniform composition of the desired polymer formula. If master-batch and compounding operations could be combined, manufacturers would save energy and time. Indeed, if the final polymer composition could be reliably formulated directly from raw materials, both master-batching and compounding steps could be eliminated.

The biggest issue preventing the reduction of number of extrusion operations is the inability to reliably control the blending and dispersion of components in a desired polymer compound. Typically, extruder systems are designed to process a particular family of polymer resins at a predetermined rate. The extruder screw (or screws) is divided into several zones to develop precise mixing conditions to allow for blending of components and to give adequate time for the components to disperse uniformly. The extruder feed system is designed to deliver a constant and uniform supply of well-mixed components to the extruder. Proper mixing and dispersion of components in a polymer blend depend on the particle size and strength of additives, polymer compound, feed system design, extruder screw design, extruder temperature profile, and extruder speed. The complexities of the interactions among these variables hinder the development of robust manufacturing procedures and complicate the diagnoses of processing problems.

Currently extruder systems are controlled by setting system variables to fixed values according to a recipe procedure provided by a process engineer. The extruder starts processing material under these conditions, and after it has been allowed to stabilize for a set time, a sample is pulled and sent to a laboratory for analysis. Extruder processing may be stopped, slowed, or continue at the set rate, according to the procedure, while the laboratory sample is evaluated. Some laboratory analyses may be complete in as little as 20 minutes, others may take as long as 2 hours. If the laboratory analyses show the product is within specification, material processing continues normally until the next sampling period. If the analyses show the product is outside of specification, the extruder operator must take corrective actions. Corrective actions might include, scrap and recycle all product produced after the last in-spec determination, adjust extruder settings to according to recommendations of laboratory or process engineer, wait for set time for process changes to stabilize, and resample product. It is not uncommon to require two or more sampling cycles to guide the process into control, with each sampling cycle typically taking more than 30 minutes.

Trends in polymer production are toward more product diversification and shorter product running cycles. A 2-hour product run, which includes a 20-minute start-up sample with adjustment, followed by a 20-minute confirmatory sample, requires the extruder to operate at nearly full power for at least 2 hours and 40 minutes, and typically produces 40 minutes (or 25%) of in-process scrap recycle.

Much of this wasted energy and time could be avoided by installing real-time composition sensors at the extruder output. The composition sensors would need to withstand the high temperatures and pressures found in extrusion systems, and would need to be nearly as sensitive and accurate as the laboratory analyses. Polymer extrusion systems can operate at temperatures as high as 425°C with head pressures up to 5000 psi (25,000 psi for injection molding machines). Typical specifications for color quality are ±0.4% for LAB readings, and sensitivities of better than 0.1%. Color is normally quantified by three values that are calculated according to procedures set forth by the International Commission on Illumination (CIE). The values are L* which is related to the perceived brightness of the color, a* which is related to red-green color balance, and b* which is related to yellow-blue color balance.

Successful demonstration of the ability to automatically control the composition of polymers from extrusion processes would in turn reduce the energy spent by in-process scrap recycle and could save energy by combining master-batch and compounding operations. The efficiency of polymer operations in the US is widely variable. Scrap recycle volume at some plants is as low as 5%, but can be as high as 40% based on our internal market research. Some of the variably may be explained by accounting differences, but most of the variability is probably due to differences in final product specifications. Tighter specifications lead to larger recycle loop volume. We estimate that between 5% to 10% of extrusion processes in the US operate under tight specifications and that they would realize an average of 20% benefit from automatic feedback control. Master-batch components are typically 5% to 15% of feed of compounding operations. The combination of master-batching and compounding operations would then save 5% to 15% energy because both processes have similar power requirements.

Using the low values for the assumed energy savings:

6% of US industrial consumption due to plastics production
5% of polymer extrusion operations benefit from this project
20% average savings from scrap recycle reduction
5% savings from combining master-batch and compounding operations

Energy Saved as % of US Industrial Consumption = 6% * (0.05)*(0.20+0.05) = 0.075%

2. Background

The use of optical sensors for process measurement and control has been an area of growth for the last several decades. This field of study is often called “process analysis” with the underlying field known as PAT or “process analytical technology”. The growth of this measurement technology is driven in part by the need for manufacturing productivity improvements. Historically process measurements involved simple univariate sensors such as temperature and pressure. More complex analysis techniques are now routinely employed in many industrial processes. (Bakeev, 2010) Spectroscopic methods of analysis that were once carried out only in laboratories can now be performed in online situations with real-time measurement for use in process control. For example, in the oil refining industry the use of NIR spectroscopy for online measurement and control of fuel properties such as Octane Number is standard practice. These online optical methods make use of robust optical probes that are inserted directly into the process, whether it is a pipe, reaction vessel, or other process components. The optical probe is connected to a spectroscopic monitoring device

using fiber optics. The particular measurement configuration is determined by the spectroscopic measurement (NIR, UV/Vis, Raman, etc). The optical probe mechanical characteristics (materials, sealing, etc) are determined by the process conditions that it must withstand.

Polymer production provides many opportunities for online process measurement. Monitoring and control of the polymerization reaction can be achieved with NIR spectroscopic analyzer systems. The additives used to achieve certain polymer performance characteristics are often monitored with UV spectroscopic methods carried out online and in real-time. In the extrusion step of polymer production, the monitoring and control of polymer color is a logical area to implement standard color measurement techniques using Visible spectroscopic methods. The concepts and methods related to color science are well known. (Gunter Wyszecki, 1982) The color of a material is conventionally defined by only three parameters, which are the coordinates in a "color space," along with the type of light source used to illuminate the material. To find these three coordinates one uses an algorithm that converts the visible spectral curve of a material into the color coordinates. (ASTM, 1996)

Process conditions that the optical probes must withstand vary widely among different industries. Typical conditions in the chemical and petroleum industries are temperatures less than 250°C and pressures below 1000 psi. Polymer extruders normally operate at higher temperatures and pressures, changing the mechanical requirements for a suitable optical probe. Standard sealing mechanisms such as o-rings are not suitable. In addition, standard unprotected silica fiber is quite fragile. To improve the fiber's strength and flexibility, it is coated with a polyimide material during the drawing process. This polyimide material is typically rated for occasional excursions to 350° C with an alternative high temperature polyimide coating that functions up to 400° C in short excursions. Additionally, industry standards for extruder wall insertion have been historically determined by the size of temperature (thermocouple) sensors and are of a narrow diameter as a result. Finally, disruption of polymer flow in the extruder by way of an optical probe extending into the flow path is typically undesirable. These process conditions and restrictions control, to a large extent, the mechanical design of the optical probe. The optical layout will also be impacted, but perhaps to a lesser extent.

As a company, Guided Wave has more than 25 years of experience working in the area of process analysis through online spectroscopic methods. The company was a pioneer in the implementation of fiber optic near-infrared analyzer systems for in-situ monitoring and control of chemical processes. Guided Wave's core business is the design, development, and manufacture of optical probes, fiber optic cables, and spectrometer systems for use in a wide variety of process conditions.

3. Discussion

The optical probes under development here will be used for measuring the color (and potentially the composition) of polymers that pass through an extruder in a blending plant. The probes will connect to one or more spectrophotometers, which will be used to measure a reflectance spectrum and in turn color coordinates. Because the measurements will be made at or in the extruder, they can be done quickly, probably in 30 seconds or less. Thus, the results of the measurements can be used to adjust the polymer blend without waiting for an off-line analysis.

Project Overview

1. Identify target polymer process
   a) A colored fully formulated product
   b) A color concentrate
   c) An additive masterbatch
2. Design probe
   a) Direct installation into the extruder is preferred
   b) The easiest way to access the extruder process is to use a probe whose tip is designed to be inserted into a tapped hole currently used for most melt temperature and melt pressure probes (Dynisco). Length of probe shaft can vary depending on the thickness the barrel or die section as well as on clearance for things like heat shields. This presents some problems for probe design due to the small diameter of the standard Dynisco port. A Dynisco M18 port is somewhat larger than the standard and will be acceptable for this use. The outlet of the extruder die will have an adapter with the M18 port to allow for optical interaction of the probe with the molten (liquid) polymer.
   c) Probes in barrel sections (along the screw shaft) will necessarily be of the reflectance type since there is no clear optical pathway through the melt (the screws get in the way).
   d) Probes in the die or in a transition between the screw tips and the die can be designed for reflectance as well as two-sided transmittance.
   e) Two options for reflectance measurements selected.
3. Fabricate probe
   a) Long lead time parts due to small quantities
   b) Precision and tolerances cause some machining difficulties
   c) Assembly issues identified for each configuration
4. Evaluate probe
   a) Lab evaluation
      (1) Optical performance verified
      (2) Calibration performance verified
      (3) Measurement algorithms verified
      (4) Temperature tolerance produced failure of window/lens braze
   b) Failure evaluation
      (1) Materials specification update
      (2) Sapphire braze process evaluation and update
      (3) Revise design drawings
      (4) Order new parts
      (5) Fabricate updated probe
      (6) Complete lab evaluation
   c) Extruder test (see accomplishments section)
5. Map extruder variables – not initiated due to schedule issues and time constraints.
6. Correlation to extruder variables – not initiated due to schedule issues and time constraints.

Color and Diffuse Reflectance

The color of a material can be determined by measuring its diffuse reflectance spectrum in the visible spectral region. Commercial instruments designed for measuring the color of paints, fabrics, or inks typically measure the reflectance at a small number of visible wavelengths and use this data to compute the color. The number of wavelengths used in such instruments usually ranges from 8 to 31, so that the spectral resolution required for these purposes is modest. The spectral range for color measurement is 400 to 700 nm. The color of a material is conventionally defined by only three parameters, which are the coordinates in a “color space,” along with the type of light source used to

illuminate the material. To find these three quantities, one uses an algorithm that converts the spectral reflectance values into the color coordinates.

The reflectance of a clear material is zero at all wavelengths. The reflectance of a black material is also zero, and the reflectance of a white material is unity at all wavelengths. Because it is impossible to distinguish a black material from a transparent one by measuring the diffuse reflectance, an auxiliary transmission measurement would be needed to distinguish between these two cases, if the process could produce either opaque, translucent or transparent materials.

Probe Design Considerations

1. **Transmission versus reflectance:**

   There are two measurement modes to be considered. In transmission spectroscopy, light is transmitted across the sample over a fixed path. The length of the path determines how much sample interacts with the light beam. The transmitted light is collected and analysed to determine how much of the light was absorbed by the sample. Transmission measurements require more probe extension into the molten polymer. Measuring the transmission spectrum of colored polymers will require a reasonably small sample path (distance between optical windows). Given the nature of the polymer stream, this would be prone to window fouling and plugging and would be very difficult to clean. In reflectance spectroscopy, the interaction of light with the sample occurs only at the end of the optical probe, over a very short distance. Light is reflected back into a collection fiber in the probe. This requires a minimal exposure into the molten polymer, thus minimizing flow disruption and also isolating some of the optics from temperature extremes.

2. **Windowed reflectance probe:**

   The windowed reflection probe involves a tight circle of 19 illumination fibers with a single return fiber in the center of the pattern. The illumination fibers are angled and angle polished so that the light from all the fibers intersect in a cone shaped pattern that fills the field of view of the return fiber. A flat window is placed over the fibers to protect them from the process polymers. The thickness of the window is such that all the optical beams from the fibers meet at the surface of the window exposed to the process. When the light interacts with the polymer in the process, some of it is reflected (scattered) back to the return fiber where it is collected and transmitted back to the spectrometer. Due to the absorption properties of the sample polymer, the return light is imprinted with the spectral properties of the sample. The geometry of the fibers and window are critical to get the beams to all coincided at the interaction point and to prevent direct stray reflections back into the receiving fiber. Any light that is returned to the spectrometer that did not interact with the sample is stray light which adds a nonlinear error to the measurement. This optical design was prototyped earlier without the protective window and was used to measure reflections spectra of powders and textiles.

   This probe design delivers more light to the polymer material and as such returns more light to the spectrometer for analysis. This provides more signal and can have a directly positive impact on the quality of the results. This probe has a flat sapphire window that is brazed to the metal probe tip. The manufacture and assemble of the nineteen fiber circular arrangement is quite challenging however and this may present a significant barrier.

3. **Hemispherical reflectance probe:**

   In this probe design there are seven illumination fibers, arranged in a circle, with a hemispherical sapphire lens brazed at the end. Because the number of fibers is odd, the sapphire hemisphere reflects a specular image of each fiber to a point in-between two fibers on the opposite side of the probe, where it is lost. A thin layer of liquid in contact with the dome scatters the incident beams, and this scattered light strikes the central pickup fiber as

the diffuse reflection. An early prototype of this design, although it was not designed for use in an extruder, demonstrated the expected optical characteristics and proved that this configuration will be useful for measurements in the extruder environment once all temperature and pressure conditions are taken into account.

Probe Construction

1. **Windowed reflectance probe:**
   Significant production issues were encountered with the brazing of the window to the probe tip. All of the prototype versions of this design experienced window failure (sapphire cracks) during the brazing process. The origin of the cracks during the brazing process appears to be unforeseen stress due to application of the brazing material in a non-uniform way.
2. **Hemispherical reflectance probe:**
   Initial prototypes demonstrated significant issues with brazing of the sapphire window to the metal probe tip. This was determined to be related to a combination of sapphire quality (degree of micro-cracks) and the sapphire surface preparation. Subsequent braze trials (with improved sapphire hemisphere lenses) proved more successful and resulted in the final construction of two probes that would be suitable for extruder trials.

4. Accomplishments

Field trials of two prototype hemispherical lensed probes were conducted in a laboratory extruder over a period of three days. Both probes were identical in configuration, consisting of a hemispherical lens with seven source fibers and one central return fiber. The fiber optic cable connecting the probe to the spectrometer was 5 meters in length. The probe is shown in Figure 1.

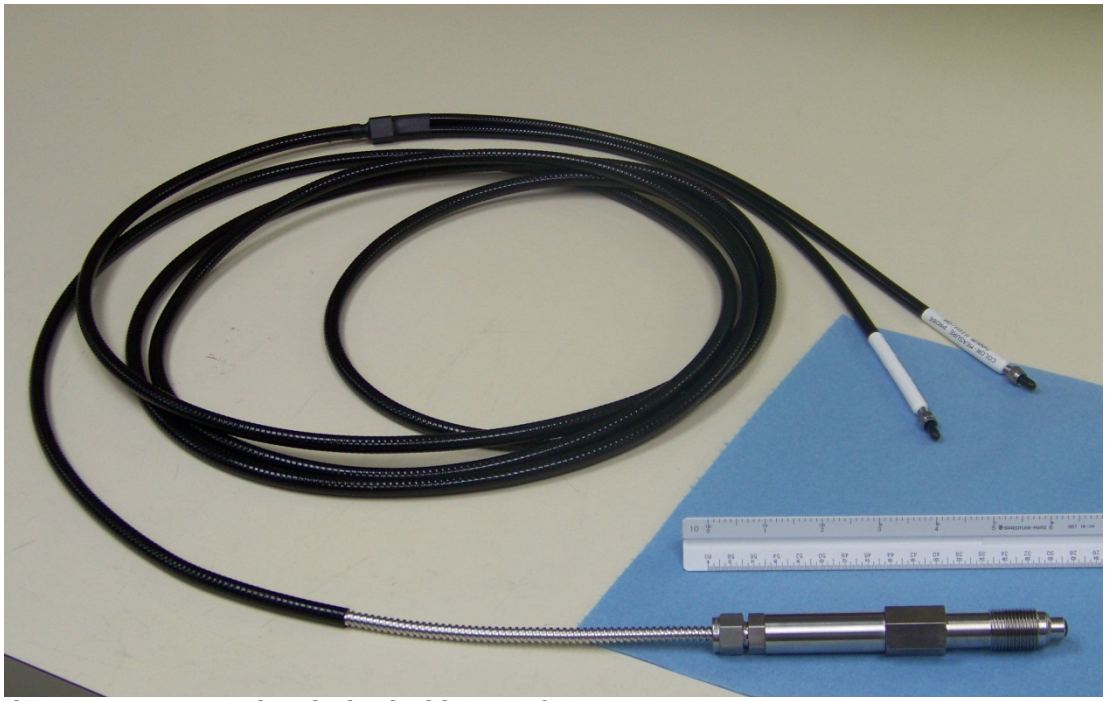

Figure 1 - Prototype hemispherical lens probe

The goals of the onsite measurement trials were to evaluate the probe measurement capabilities and mechanical robustness in a polymer extruder at temperatures up to 300°C and pressures up to 2000 psi. The optical measurements were made using a Guided Wave Model 508 UV/Vis diode array spectrometer system. The specifications of this unit can be found in the Guided Wave product literature. Some system software changes have been made to allow for the measurement of color in liquid polymers through reflectance. The resulting combination of software and hardware are given the term "Polymer Color Measurement System" or PCMS for abbreviation. The measurement of interest in the polymer extruder is Color. The units are given as CIE L*a*b*. The relevant mathematical details of this measurement are given in the appendix. The probe is designed to measure the diffuse reflectance of the colored polymer. For opaque materials most of the incident light is reflected. For transparent materials there is likely to be insufficient diffuse reflectance for measurement purposes.

Figure 2 shows the analyzer system and probe installed in the laboratory extruder (Leistritz 18mm co-rotating intermeshing twin screw) using an 18mm (Dynisco M18) port in a two strand die. At the installation point, the color components should be completely mixed to their final specification. Measurement of the color at the extruder will provide for more accurate batch control and reduced scrap levels. Figures 3 and 4 show close up views of the probe installation point.

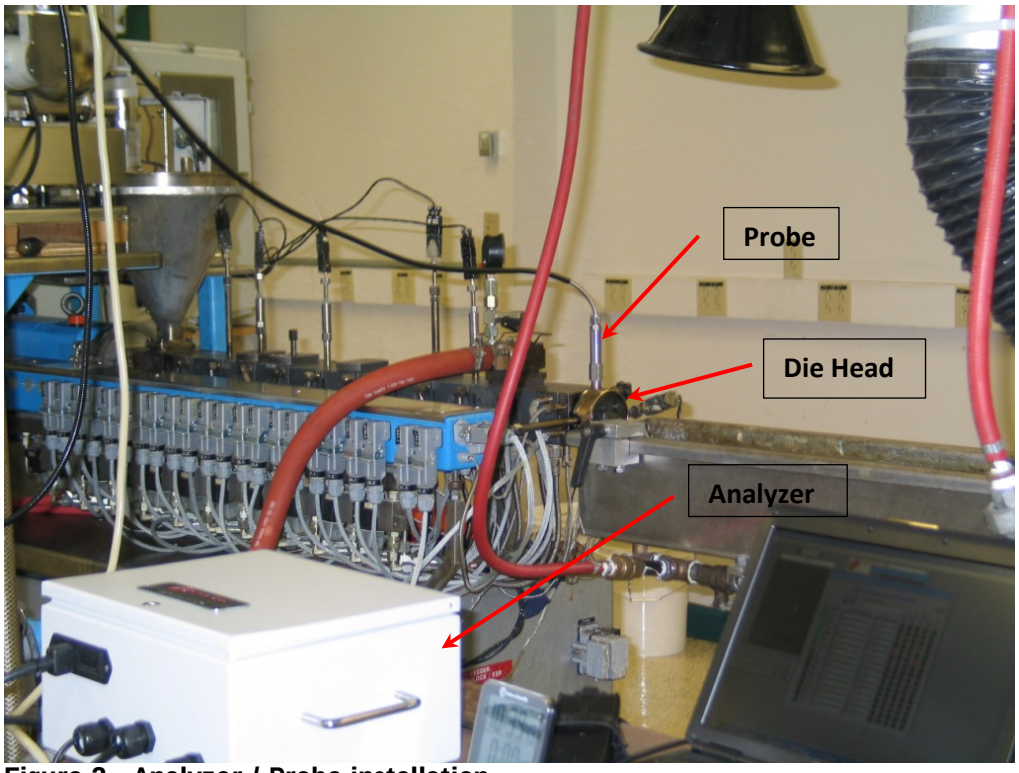

Figure 2 - Analyzer / Probe installation

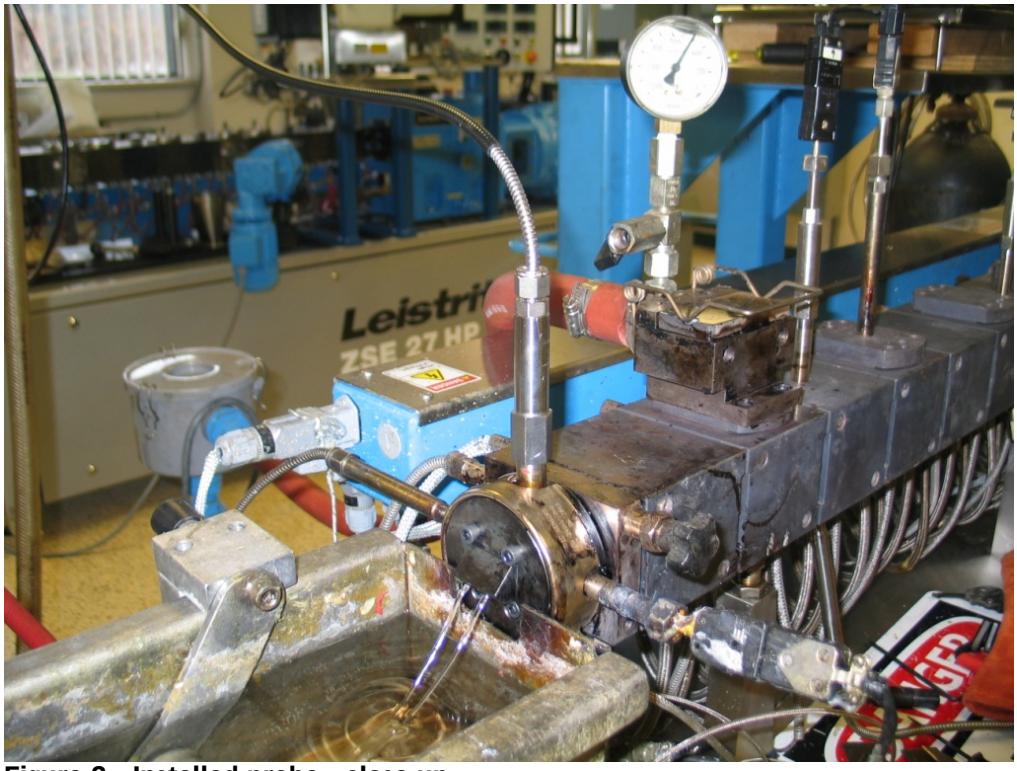

Figure 3 - Installed probe - close up

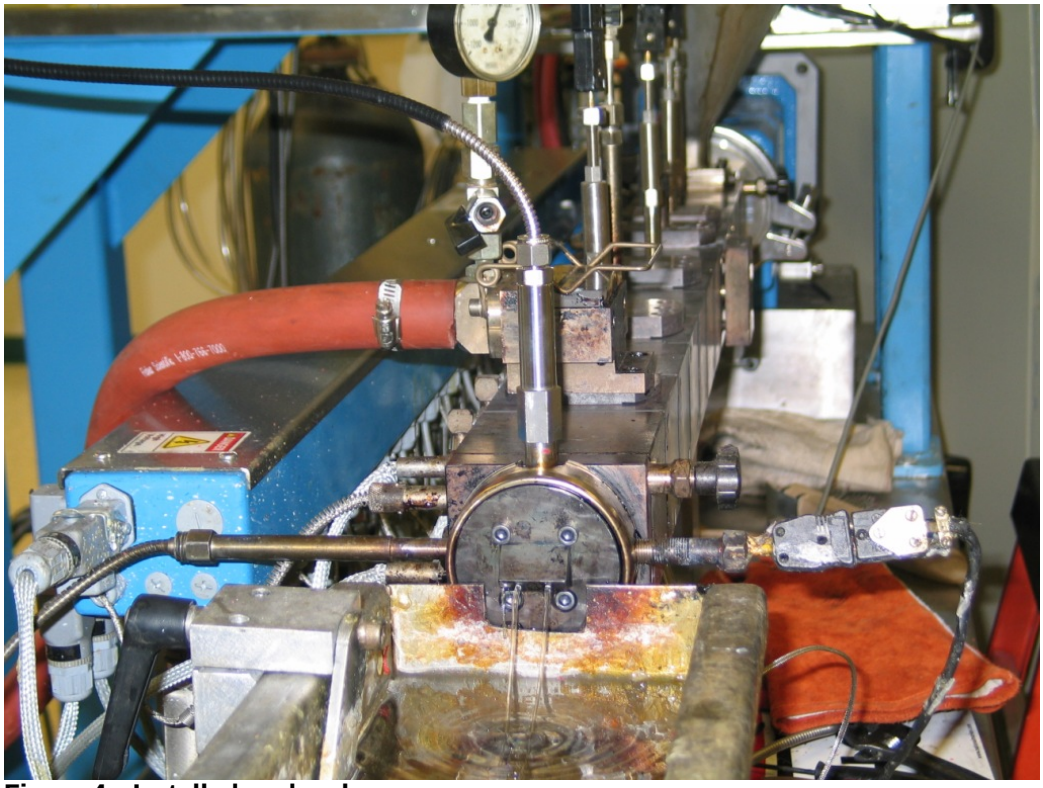

Figure 4 - Installed probe close up

The first extruder run was carried out with polyethylene. The melt temperature for polyethylene is 230°C. The extruder temperature profile ranged from 180°C at the feeder location up to 230°C. Each scan collected consisted of eight co-added scans with 600 lamp pulses per scan. The approximate measurement time is 45 seconds. Polyethylene was introduced into the extruder with no colorant. In the melt state the polyethylene is clear. Figure 5 shows scans of the empty extruder and during measurement of clear polyethylene. The y axis scale is in percent transmission (%T) and the X axis scale is in nanometers. Both measurements are similar in scale, indicating that little reflectance is seen from the clear polyethylene material with the primary signal being a result of stray light. Figure 6 shows continuous spectral measurements of the clear polyethylene material over an approximate one hour period with measurements made every 45 seconds.

A red colorant was introduced into the extruder with the target of 3% loading for the final product. The final product is opaque. Transition from the clear to fully colored polymer was rapid, and the 45 second measurement time precluded the observation of color increase. The spectral features associated with the colorant are easily visible as seen in Figure 7. The colorant was removed from the extruder and the addition repeated at 1.5% loading and 2% loading. The calculated L*a*b* values for the polyethylene runs are shown in Figure 8. In this figure the X axis is time. Ultimately it will be necessary to determine the agreement between the online measured color values and an offline laboratory color value measured on a solid sample. While material was collected from the red polyethylene experiments, no color values have been received related to this solid material.

At the end of the polyethylene runs, the probe was removed for examination. The polymer solidified on the end of the probe surface when cooled. Removal of the solid polymer was not possible with typical solvents, so the probe tip must be cleaned when hot, taking care to remove any residual polymer from the end. Inspection of the probe tip after the conclusion of the runs showed no cracks or other issues with the sapphire. There was some discoloration on the fiber holder.

Figure 5 - Red trace is empty extruder, blue trace is clear polyethylene

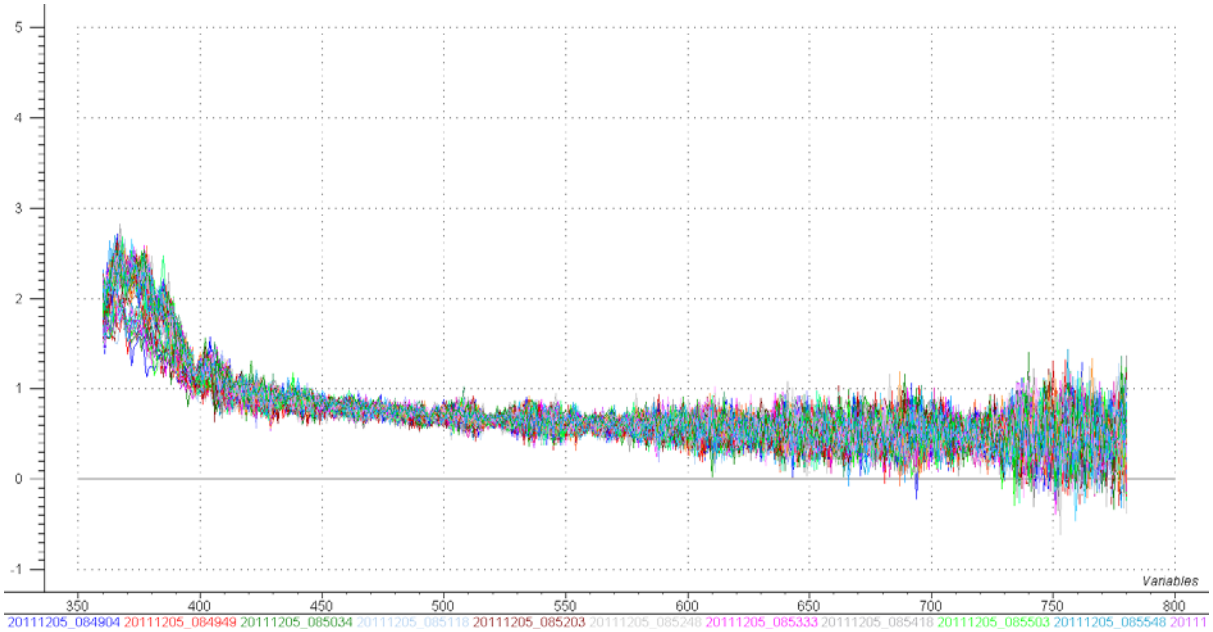

Figure 6 - Clear polyethylene, one hour run

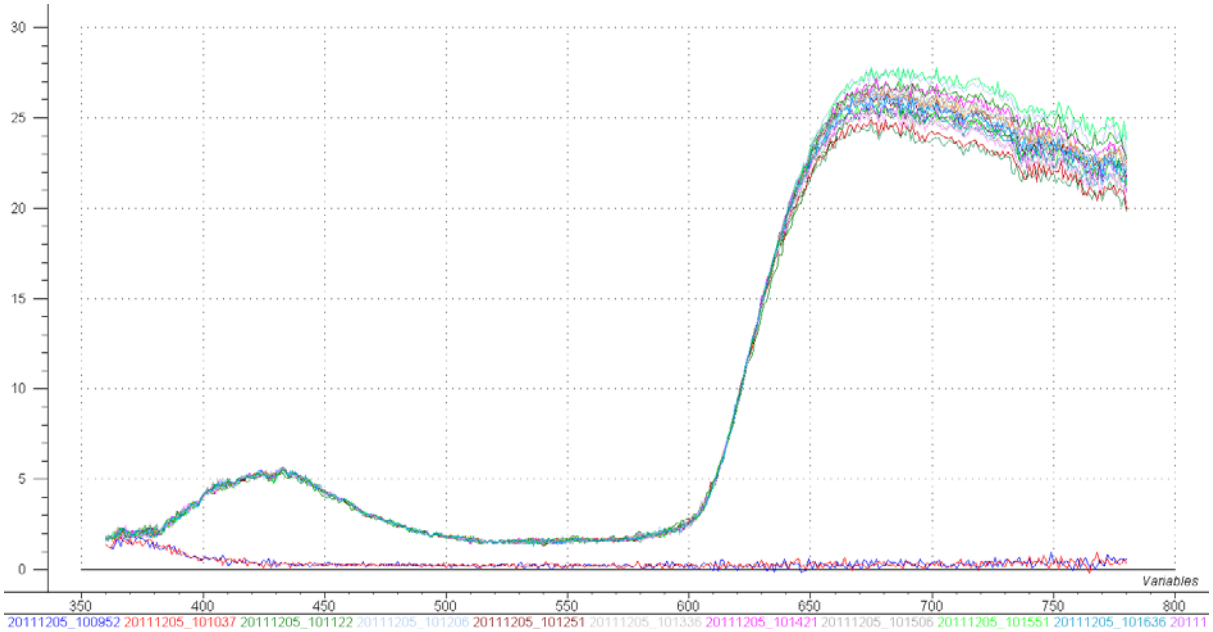

Figure 7 - Red colorant in polyethylene

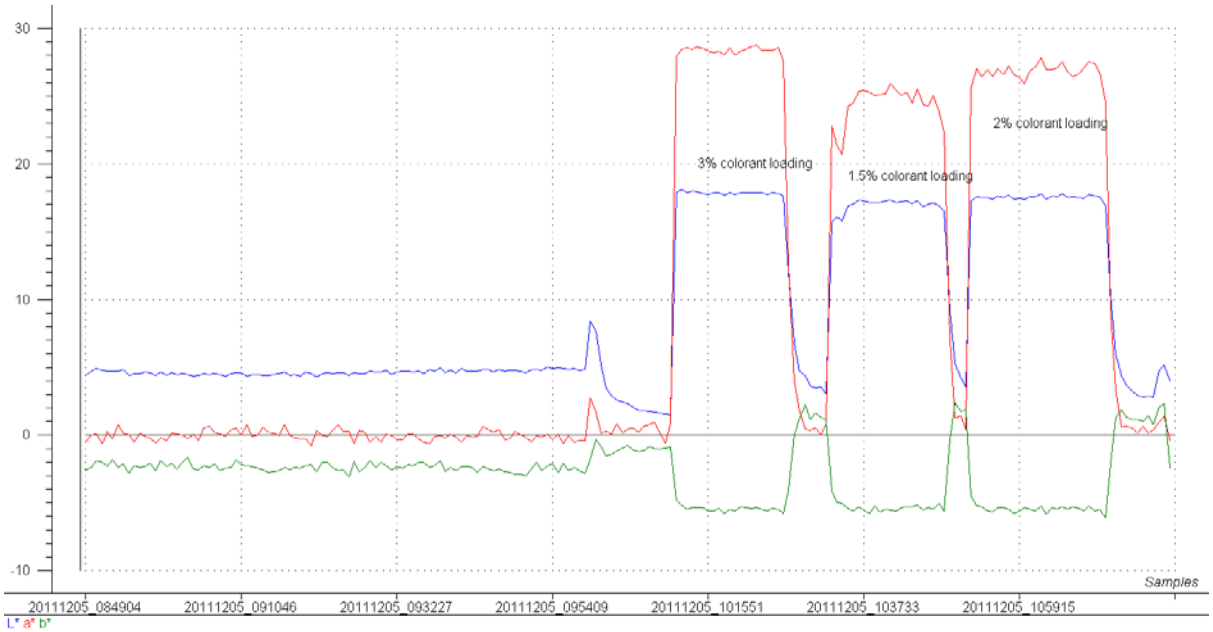

Figure 8 - CIE L*a*b* color values

For the second day of trials, a polyester resin was selected for measurement. The selected polyester has a melt temperature of approximately 285°C. The operating pressure for the extruder was between 800-900 psi. A transparent red color concentrate was selected for measurement. The final product is translucent red. This polymer configuration produced a more challenging measurement. There is not sufficient reflectance produced from the translucent material to measure the color value. Figure 9 shows the CIE L*a*b* for the following:

1. Addition of transparent red colorant to the polyester
2. Increase of colorant by factor of 3

3. Addition of some opaque red polyethylene
4. Use of blue colorant with polyester
5. Addition of titanium dioxide (TiO2) to the blend with blue colorant
6. Addition of titanium dioxide to the blend with red colorant

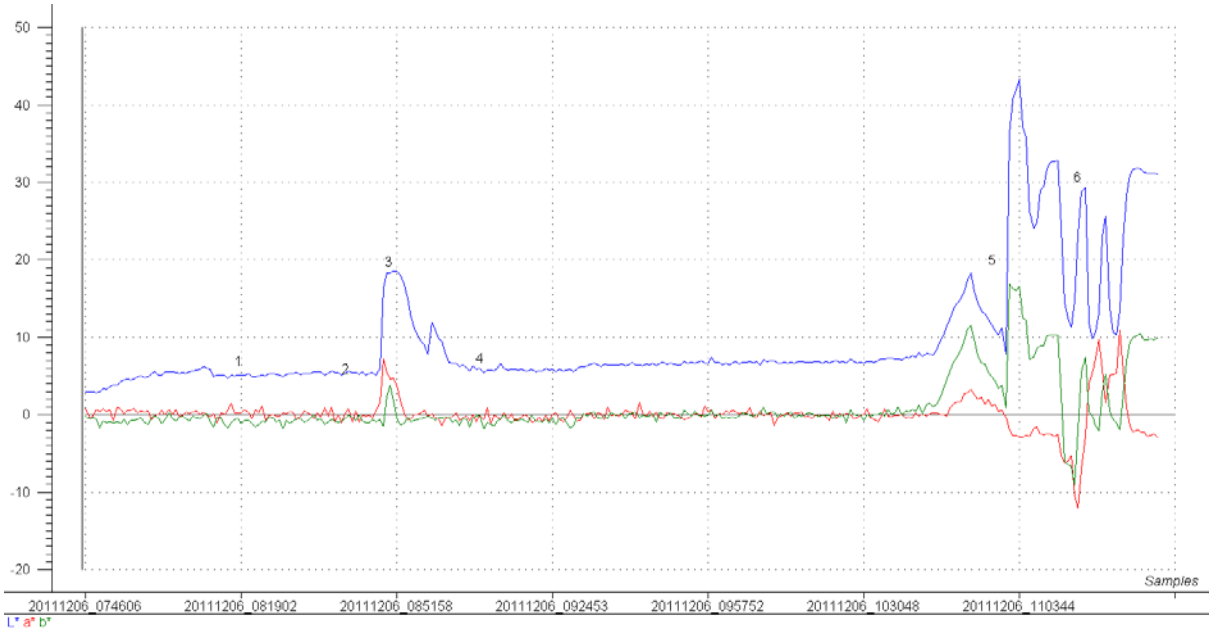

Figure 9 - Polyester, L*a*b* color values

The results from the polyester run show that the color measurement via reflectance will not be feasible for translucent materials. In those cases a configuration incorporating a true transmission measurement will be required. The addition of TiO2 or some other opaque material will provide enough reflecting surface for a color measurement to be made via reflectance.

A third polymer material was explored –poly butylene terephthalate (PBT) which has a melt temperature of 260°C. PBT is a semi-crystalline polymer that is a type of polyester. A short run of the PBT adding blue colorant followed by red colorant was conducted. The color values for this run are shown in Figure 10. The colored PBT is opaque.

At the conclusion of the extruder runs the probe was removed and examined. It appeared that the center (return) fiber had broken at some point in the probe. When dis-assembled, it was revealed that the fiber pulled free from the fiber holder at the tip of the probe. The most likely cause of this is the twisting during installation / removal of the probe. The center fiber has little to no give and will be much more susceptible to the forces applied.

Trials on day 3 were originally scheduled to investigate any potential differences between dye colorants and pigment colorants. The alternate probe was installed and verified to be in working order. The initial run was set with polyethylene and the original red colorant. Figure 11 shows the color measurements from this material. A computer

failure caused the software to halt and it became necessary to remove the probe from the extruder to collect a new system reference. Removal of the probe caused the center fiber to break free on the second probe and no further data collection was possible.

Comparison of online results of L*a*b* values with the offline results measured on solid polymer plaques showed that the L* value measured on the solid plaques was higher than the L* value measured in the melt. This can be attributed to the increase in opacity on crystallization. The results also suggest a color shift with temperature of the sample in the melt when compared to the solid plaques (b* values). These differences between the measurements made in the polymer melt and the molded plaques are consistent with known behaviors of pigments in polymer systems. These are challenges for using online measurements in the melt where many different types of colors and polymer systems are used. It may be necessary to generate correlations between spectra for the melt and solid material to predict comparable final L* a* b* color values using a polymer melt probe.

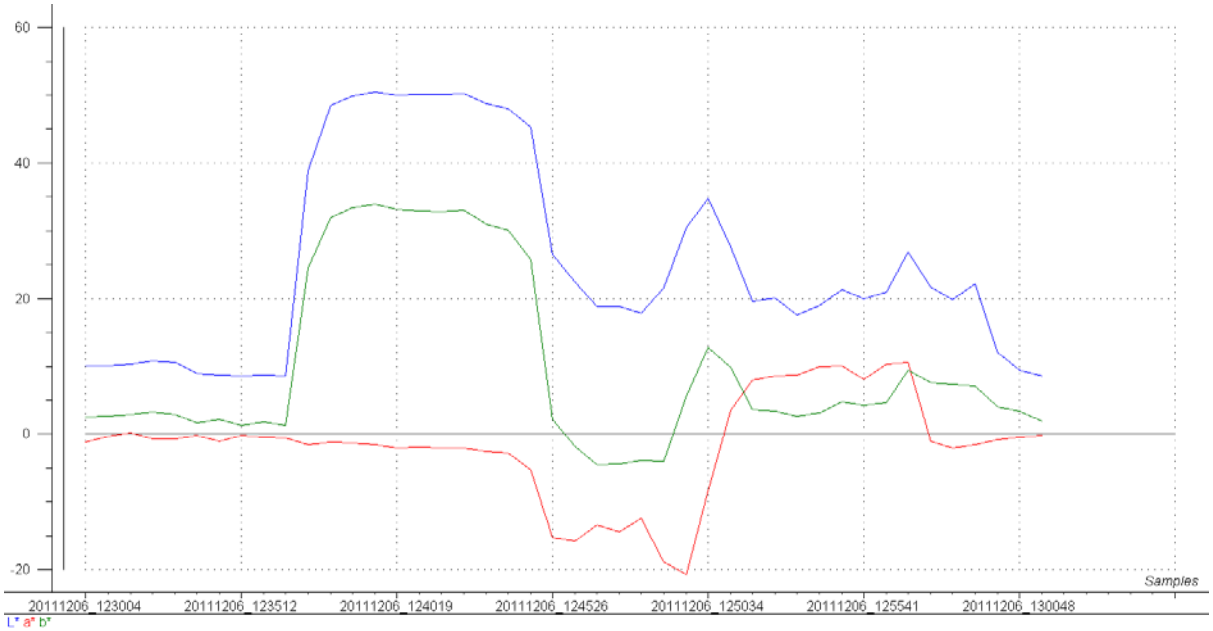

Figure 10 - BPT L*a*b* values

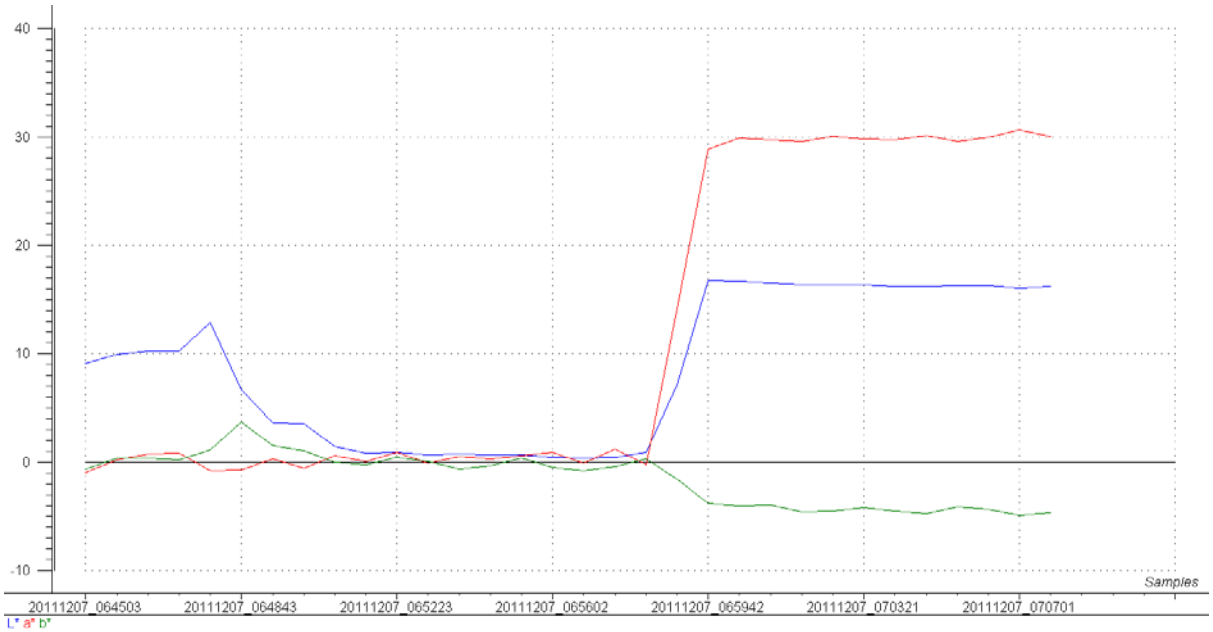

Figure 11- Polyethylene L*a*b* values, alternate probe

On return to Guided Wave, both probes were disassembled to explore the damage incurred during the trials. In both cases the center fiber broke free from the fiber holder. This was likely caused by high stress placed on the fiber during the installation / removal process. In addition, a lateral crack in one of the sapphires was observed. The cause of the lateral crack is unknown.

Future improvements to the probe design will include the separation of the long fiber cable (8 fibers) from the probe body itself. This will require an individual fiber attachment for both the source and the detector fibers in the probe. One configuration under consideration is shown below in Figure 12. The fiber "pig-tail" at the end of the probe is only a few inches in length, allowing individual source and detector fiber cables to be attached to the probe after installation, thus removing the source of stress on the individual fibers inside the probe body.

Two other improvements are under consideration. First, the stainless steel part the fibers are glued into can be replaced with ceramic. This will provide a better temperature coefficient match between the fibers and their holder. The second change is to separate the threads from the body of the probe. A male nut would be added to compress the probe into the Dynisco port thus permitting the probe to be inserted and removed without twisting.

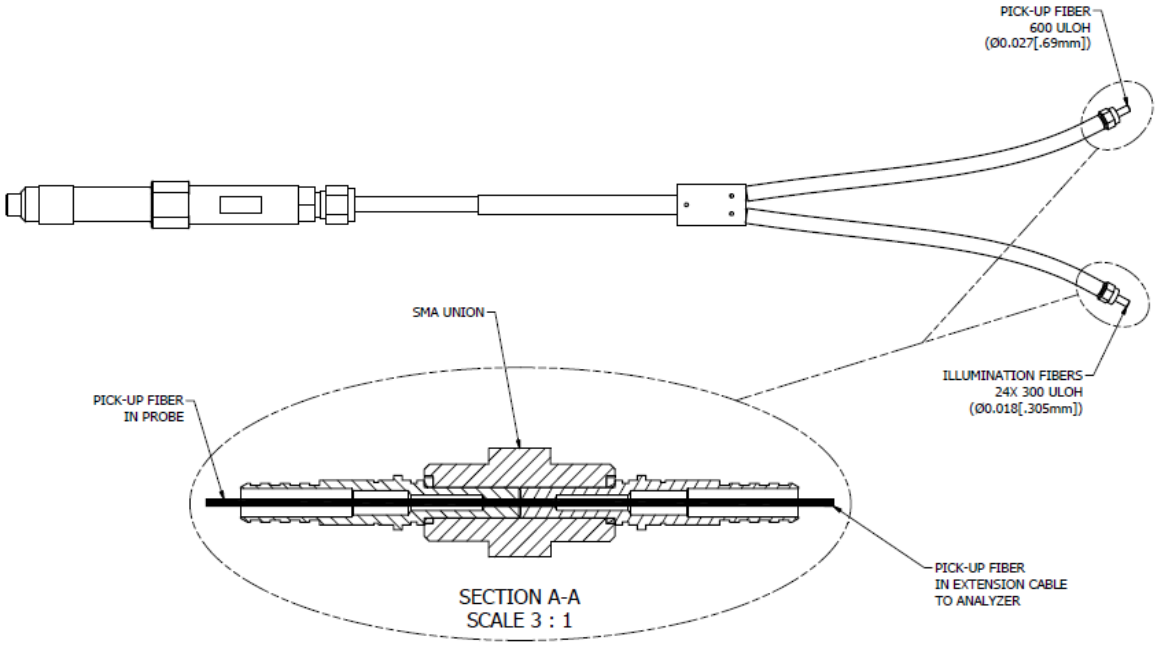

Figure 12 - New proposed fiber connection

5. Potential Benefits Assessment

As mentioned earlier, the 2003 DOE report, "U.S. Plastics Manufacturers Stand to Save Energy, Boost Competitiveness, and Reduce Costs", states: "The plastics industry consumes approximately 6% of all the energy used by U.S. industries, and it is valued at $6 billion (based on 1998 DOE and other data). DOE estimates that reducing the plastics industry's energy use by even 1% by 2010 could shave at least $100 million from its total annual energy costs."

In polymer extrusion, once the production cycle is complete, off-spec product is either recycled back through the process for re-work, or scrapped. While rework will result in little material being wasted, all of the energy and processing time are lost. In the case of scrapped material, both the material and the energy costs are lost. Estimates of the size of the internal recycle loop range from 5% to over 40%. Eliminating a portion of this recycle (rework) will result in significant energy savings. Reducing scrap will provide both energy and material savings. Online sensor systems capable of reducing product variability will in turn increase the first pass yield (reducing rework and scrap).

The data collected during this project demonstrates successful online polymer extruder color measurements that can be used to optimize production and reduce product color variability. The fast response time achieved is a good indicator that production time can be reduced by having real time measurements of when product specification is met thus shortening the startup time.

If only energy savings from recycle and scrap reduction is considered:

6% of US industrial consumption due to plastics production
5% of polymer extrusion operations benefit from this project (estimate)
20% average savings from scrap recycle reduction (estimate)

Energy Saved as % of US Industrial Consumption = 6% * (0.05)*(0.20) = 0.06%, or approximately $6 million saved just in energy costs.

True measures of the energy savings will require further study involving the mapping and study of extruder variables for color monitoring.

6. Conclusions

Successful online polymer extruder color measurements were made with a newly designed and fabricated hemispherical lensed diffuse reflectance probe that employed 7 illumination fibers and one collection fiber. The color measurements were made by way of an existing diode array UV/Visible color spectrometer system. The probe/spectrometer responded rapidly to changes in the color of the polymer melt. Stagnation of the melt on the probe tip was not seen as a significant issue in these trials.

Challenges in the design and fabrication of the probe included:

1. Size – extruder geometry limited the port size for the optical probe
2. Brazing – mechanical attachment of sapphire to metal was difficult to achieve while maintaining crack-free sapphire
3. Temperature – the temperatures experienced in the extruder are near the limits for some internal components of the probe
4. Pressure – high pressures experienced during extruder operation must be tolerated
5. Efficiency – low light levels from reflectance measurements means that optical efficiency is of key importance.
6. Stray light – theoretical mechanisms for correcting for stray light were necessary
7. Calibration mechanism – because this measurement is not done in a typical way (for color) where a color standard is measured prior to a sample is measure, a reliable color calibratoon mechanism had to be developed

These challenges were met, but materials issues and methods of construction sill require improvement for continued work on this front.

7. Recommendations

Additional work is required to address the issues related to:

1. Sapphire to metal brazing techniques – the yield on the brazing process needs to be improved before production can be attempted.

2. Light loss resulting from multiple fiber connections required for the bundled fiber approach.
3. Correlations between liquid and solid color. Data is required to determine if this is a polymer specific correlation or if it is only related to opacity differences.
4. Calibration mechanism improvements for routine use.

8. References

ASTM. (1996). *ASTM Standards on Color and Appearance Measurement.* West Conshohocken: ASTM.

Bakeev, K. A. (2010). *Process Analytical Technology.* Chichester, UK: Wiley & Sons.

Gunter Wyszecki, W. S. (1982). *Color Science.* New York: John Wiley & Sons.

9. Appendices

ALGORITHMS

Stray-light correction

The equations below are applied to the spectra on a wavelength-by-wavelength basis. The raw reflectance is converted to the stray-corrected reflectance, R_{sc}, by subtracting the stray light and correcting for the actual reflectance of the standard according to the equation

$$R_{sc} = (R_{raw} - R_{cpa}\, f_{ri}) \frac{R_w}{(f_{so} R_{std} - R_{cpa})} \quad . \tag{2}$$

The variable f_{so} is the standoff-distance correction factor defined in the "Factory Setup" section, and f_{ri} is a refractive-index correction factor defined by

$$f_{ri} = \frac{\left(\frac{n'_e - n'_p}{n'_e + n'_p}\right)^2}{\left(\frac{n'_e - 1}{n'_e + 1}\right)^2} \quad . \tag{3}$$

Here n'_e and n'_p are the refractive indices of the optical element that forms the probe tip and the polymer, respectively, at the temperature of use and the wavelength of interest. When a solid is being tested, the medium in contact with the probe is air, $n'_p = 1$, and the above equation reduces to $f_{ri} = 1$. Also, when a solid is tested, the software assumes that it is placed at the factory-set distance from the tip of the probe, so that $f_{so} = 1$ at all wavelengths. The factory-set distance is specified in the "Factory Setup" section, and is currently equal to 0.004 inches.

If the operator has chosen not to correct for stray light, the software sets $R_{cpa} = 0$, and equation (2) is replaced by

$$R_{sc} = R_{raw} \frac{R_w}{f_{so} R_{std}}. \tag{2a}$$

when a liquid is tested, and by

$$R_{sc} = R_{raw} \frac{R_w}{R_{std}}. \tag{2b}$$

when testing a solid.

Equation (2) gives the reflectance of the sample, corrected for the distance of the reflectance standard from the probe during calibration, the distance of the sample from the probe during use, the actual reflectance of the calibration standard, and the presence of stray light. Equations (2a) and (2b) replace equation (2) when stray light correction is not done.

Correction for difference between usage conditions and calibration conditions

If the sample is a liquid, the program converts R_{sc} to the calculated reflectance of a solid sample in air, as follows. The latter reflectance is given by

$$R_a = R_{sc} T_{es} / T'_{ep} \,, \tag{4}$$

where T_{es} and T'_{ep} are defined by

$$T_{es} = \left[1 - \left(\frac{n_e - 1}{n_e + 1} \right)^2 \right]^2 \tag{5}$$

and

$$T'_{ep} = \left[1 - \left(\frac{n'_e - n'_p}{n'_e + n'_p} \right)^2 \right]^2 \tag{6}$$

Here T_{es} is the double-pass transmittance of the probe-air interface during calibration, and T'_{ep} is the double-pass transmittance of the probe-polymer interface during use. Also, n_e is the refractive index of sapphire at the calibration temperature, usually 20° C. The primed quantities are measured at the temperature of use. If the sample is a solid, equation (4) reduces to $R_a = R_{sc}$. The reflectance R_a is the reflectance spectrum of the sample in air at the temperature of use, after correcting for stray light and for the difference between the reflection losses during use and the reflection losses during calibration.

For possible use by the operator, the program stores R_{sc} and R_a in Model 508 disk files named "Stray-corrected.gva" and "Final spectrum.gva," respectively. To not put a large number of files on the disk, these two files are overwritten each time a scan is done. Thus, they represent the most recent scan.

Determination of refractive indices

To find the refractive index for a material at a specific wavelength and temperature, *t*, the program uses the Conrady equation and the stored Conrady coefficients of the material at 20° C and at 300° C. Since *t* may not be exactly 20° or 300°, the program uses linear interpolation or extrapolation of the refractive index data at the given wavelength to find the refractive index at the temperature *t*. This process is repeated for all of the wavelengths.

Color calculation

After finding the final spectrum R_a, the software converts R_a to the CIE L*a*b* color for a specified illuminant and a specified CIE observer. By default, the illuminant is D65 and the observer is the 1964 10° observer. The software finds L*, a*, and b* by using the algorithms defined in ASTM E308-06, "Standard Practice for Computing the Colors of Objects by Using the CIE System" (ASTM International, W. Conshohocken, PA, 2006). The program uses 380 and 780 nm as the integration limits, with a 5-nm step size.