Benefits of Real-Time Color Measurement in the Melt Stream

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Abstract
The measurement of the color of molten plastic prior to extrusion offers a number of advantages and benefits for color quality, as well as for extruder diagnostics. Making the measurement farther 'upstream' allows for more rapid and effective response or correction to color drift or out-of-tolerance conditions. Real-time color data can also be used to diagnose extruder conditions such as color feeder performance and screw speed / wear. Furthermore, this real-time data is required if one is to 'close the loop' and allow for automated color corrections.

Background Information
The goal of process analytical technology has been to move the measurement of key physical parameters (e.g. temperature, concentration, pressure, color) out of the laboratory and as close as possible to the production line.[1] Measurement of plastic samples in the lab often requires preparation of the sample that delays the lab's response to the production floor's request for information.[2] Also, the process of collecting, processing, and measuring samples limits the number of samples that may be used to characterize or provide quality control of a product.[3]

The first report of online color measurement in the melt was by Calidonio.[4] Advances in technology since then have improved the quality of this measurement[3] and made it a realistic option for inclusion in the suite of online measurements that an extruder or injection molder may employ.

Objective of work
The objective of these tests was to demonstrate the measurement of color in molten plastic for the purpose of controlling that color, and to show that these color measurements also yield information about other aspects of extruder performance.

Experimental procedure
<u>Equipment</u>

All data was collected using a fiber-optic spectrophotometer with a CCD detector and xenon flash lamp (Online Color Spectrophotometer, Equitech Int'l Corp., New Ellenton, SC). The instrument functions as a double-beam spectrophotometer, with a probe or sample channel and a reference channel. Two different fiber-optic melt probes were used: one for reflectance spectroscopy (Reflection Polymer Melt Probe, Equitech Int'l Corp., New Ellenton, SC) and one for transmission spectroscopy (Transmission Polymer Melt Probe, Equitech Int'l Corp., New Ellenton, SC). The probes are designed to fit into a standard ½-20 UNF extruder port that is typically used for temperature or pressure transducers. The materials in contact with the process are the sapphire window and Hastelloy® probe tip. All color data were computed from spectral data using illuminant D65 and a 10° observer function. The optical geometry of the reflectance probe was 28°/0°. The instrument can achieve a stability of 0.2 units L*, a* or b* per day. All testing was done on twin screw extruders.

<u>Installation</u>

The installation location for the probes for each test was carefully planned to achieve optimum results. The probes must be placed in a region of good material flow with high shear. This helps refresh the material at the probe window and minimize the chance for coat-over of the optics. An additional consideration for transmission spectroscopy is that the gap between the input and output probe windows be small enough to allow adequate light to be transmitted through the melt stream. The die lip can be an excellent installation location for both transmission and reflection work, although other locations can be successful as well. For example, a reflection probe can be installed in an adapter between the extruder and the die.

Experience has shown that it is best to have the probe tips protrude into the polymer flow slightly, to avoid any stagnant or slow moving material right at the adapter wall. For this work, each probe tip penetrated approximately 2.5 mm past the adapter wall.

Choosing the correct gap or optical path length between the transmission probe bodies is essential to a good measurement. If it is too great, inadequate light may be transmitted, or variations in the optical characteristics of the flowing polymer can add instability to the signal. If the gap is set too small, then sensitivity to changes in the system is reduced.

<u>Transmission Calibration</u>

The instrument and probe can be calibrated in 3 different ways for transmission measurements, depending upon the way in which the extruder is operated. One method of calibration is to fill the extruder with clean resin, omitting colorants, and use this as the basis for the 100% transmission line. Sometimes color variations in the base resin preclude this approach. If it can be guaranteed that the extruder is empty with no residue on the optical windows, then a 100% transmission line can be measured *in-situ* through air. In this case, once plastic is flowing, improved optical coupling can cause light throughput to increase, leading to L* values greater than 100. If neither of these options is possible due to the nature of the extruder or extrusion process, then the fiber assemblies can be withdrawn from the melt probe bodies and installed in an external calibration fixture. The 100% transmission line is determined in this fixture and the fiber assemblies are replaced in the melt probe bodies on the extruder. Like the second calibration method, this method can also result in L* values greater than 100 once the polymer is flowing between the probe windows.

<u>Reflection Calibration</u>

For reflection measurements, the instrument and melt probe are calibrated by withdrawing the fiber assembly from the melt probe body and placing it into an external calibration fixture. A black trap, white tile, and green tile may be alternately attached to the fixture as needed during the calibration procedure.

Discussion of data and results

<u>Reflection</u>

Extruder Start-Up

As an extruder run begins, there is always some lag time while the system attains stability and the desired product color is reached. Online color measurement can give the operator a valuable tool for following this process. For example, in Figure 1, it can be seen that approximately 12 minutes passed from start-up to stable color during the production of tan polypropylene.

Sensitivity to Color Contaminants

The sensitivity of the color measurement can be seen by the intentional addition of contaminants into the material flow. Figure 1 shows a run of tan polypropylene as various color contaminants are added to the extruder, resulting in responses in all three color coordinates. Between 0.25 and 1.5 g of ‘contaminant’ color chips were added and the response was observed. In all cases, some response was detected, with

0.25 g of white having the smallest effect. These amounts represent a loading of approximately 0.1% contaminant for this test. In actual operation, these color variations could come about through material holdup from an earlier run, or a stray color chips coming from the feeder.

Repeat Runs of the Same Product

Polyethylene with 4 colors was run on a 43-mm twin-screw extruder. Each color was run twice on each of two days. The results of these measurements are shown in Table I. An important aspect of online color measurement is that the actual color values will, in most cases, not match the numerical values that might be obtained from a laboratory measurement. This is primarily due to differences in measurement geometry, sample temperature, and sample preparation. Furthermore, the acceptable delta E in the online values may be higher than that in the laboratory, due to process variations that are detected online, but in the end still result in an acceptable product.

Differentiating Similar Products

Monitoring the extrusion process in the melt gives a measure of the product's color, as well as showing other features of the extrusion run. Figure 2 shows the L*a*b* plot for a 2.5 hour run over 2 different white polypropylene products. Product B was repeated to demonstrate the ability of the probe to report similar values for the same product over a second run. Significant events that are apparent on the plot are purging of the extruders between product runs. Two smaller perturbations in the measured b* value were found to be correlated to issues with the proper refilling of one of the feeders for the extruder.

Titanium Dioxide Loading / Feeder Diagnostics

The effect of titanium dioxide loading on the L* value of ABS polymer can be seen in Figure 3. In this test, TiO_2 loading was changed from 4% to 8% to 2% and finally back to 4%. Variations in the feeders can be seen as a ripple in the measured L* values.

With the ability of frequent measurements also comes the capability to measure feeder performance. Many feeders today, even with their gravimetric capabilities, cannot always assure homogeneous dosing. When a feeder has multiple components there is a possibility of denser material settling to the bottom of a particular dose. This can result in an oscillation of the color values that can be measured online. Since these oscillations can happen several times per minute, off-line measurements would not be able to point to the feeder as the cause when inconsistent product is produced.

Color Control

Online color measurement allows for the possibility of real-time feedback and control of product color. This is demonstrated in Figure 4. Here, gray PET is being produced from recycled materials with wide variation in color. Pigment is added to bring the melt to the target gray; automatically making small adjustments to the feeder based on the reported L* from the online instrument. Closed loop control is only possible where a measurement can be made in the process.

Other Diagnostics

Online color measurements can indicate problems with components of the extrusion line other than the feeders. Changes in color detected by the measurements can alert the operator to check heater bands for inconsistent heating, screws for wear leading to inconsistent mixing and even point to inconsistent drying of hygroscopic resins. Optimal screw speed can also be determined on color stability – too fast leads to degradation of the material and too slow leads poor mixing.

Transmission

Extrusion -Injection Molding (Pre-Form Bottles)

Although pressures attained in injection molding often exceed the limit of the probes used in this study (6000 psi), careful placement of the probes in a lower-pressure region of the machine can allow for their use. In this case, transmission probes were installed in a barrel-head adapter that leads from the extruder down to the higher pressure injector into the mold. A valve protects the extruder from the higher pressures reached during the injection cycle. The application is the production of green or blue PET pre-forms for drink bottles. Figure 5 shows the L* response of the probes as the material changes from recycle feed with an L* of about 40 before green pigment is added to an L* value of about 14 after the pigment addition. The data shows that the target color is reached in only about 5 minutes from the start of pigment addition, and thus when acceptable pre-forms may be pulled and packaged for shipment.

Sensitivity to Color Contaminants

In this test, black color chips ('contaminants') were intentionally added to a batch of molten polystyrene. Three different additions in decreasing amounts were carried out: 0.5, 0.25 and 0.125 g. The results of this can be seen in Figure 6. In this test, the transmission probe windows were16 mm apart. All three material additions were easily detected. This is important, as it would allow for immediate warnings to the operator that something was wrong with the process and allow for repairs and/or corrections to be made in a timely fashion.

Tracking Process Color

The b* value for a PET run was tracked over a 3-day period with frequent sampling and laboratory testing. The laboratory and process b* values are shown in Figure 7. The online data follows the trends in the laboratory numbers quite well. It may be possible to develop a correlation between the online and laboratory results for a product, as long as factors affecting online color are taken into account for each recipe. Figure 8 shows a simple linear best-fit line for the b* data from Figure 7.

Conclusion

For any process, measurement of key parameters is important for predicting results. For many processes online color measurement can be an important input in determining productivity. By using this real-time data effectively, a process can be improved better than by inspecting relatively few samples after the product has been produced. In other words, instead of off-line inspection, the color can be statistically sampled in a cause-effect relationship through the process. Improvements include better mixing, better feeding, and elimination of post blending.

The use of online color measurement to provide real-time control of color is just beginning in the plastics industry, but many benefits can already be seen. Technology will continue to move forward, no doubt, towards the ultimate goal of closed loop color control.

Acknowledgements

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References

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3. "In-Line Color Measurement Directly in the Melt"; Eker, Fuat; *Kunstoffe international*, 4/2009, pp. 35-37 translated from *Kunstoffe* 4/2009, pp. 54-56.

4. "In-Line Color Measurement of Pigmented Polyethylene During Extrusion"; Calidonio, F.; B. A. Sc. Thesis, University of Toronto, 1995.

Illustrations, tables and figures

Table I. Measured color values over 2 days for polyethylene.

Product Color	Test Day	Elapsed Time (min.)	L* avg	a* avg	b* avg	L* St Dev	a* StDev	b* StDev
Yellow	Day 1	29	29.08	8.41	16.71	0.06	0.07	0.27
Yellow	Day 1	16	29.60	9.33	19.30	0.16	0.06	0.12
Yellow	Day 2	15	28.85	9.37	19.75	0.15	0.10	0.14
Yellow	Day 2	18	28.46	9.86	20.05	0.10	0.08	0.15
Gray	Day 1	23	26.50	3.35	4.10	0.13	0.03	0.06
Gray	Day 1	14	26.25	3.43	4.97	0.13	0.04	0.13
Gray	Day 2	16	25.59	3.52	5.42	0.21	0.07	0.16
Gray	Day 2	15	25.26	3.98	5.44	0.05	0.02	0.08
Dark Red	Day 1	21	16.25	9.40	7.00	0.11	0.07	0.25
Dark Red	Day 1	20	16.02	9.42	7.78	0.11	0.09	0.22
Dark Red	Day 2	14	15.78	9.49	8.20	0.11	0.06	0.23
Dark Red	Day 2	14	15.90	9.45	8.87	0.11	0.06	0.22
Gray-Blue	Day 1	27	16.94	2.59	-2.82	0.42	0.95	1.25
Gray-Blue	Day 1	26	16.60	1.94	-2.81	0.67	0.26	0.67
Gray-Blue	Day 2	23	15.91	1.93	-2.65	0.71	0.32	0.59
Gray-Blue	Day 2	24	16.09	2.23	-1.56	0.86	0.21	0.91

Figure 1. Tan polypropylene with various color contaminants added.

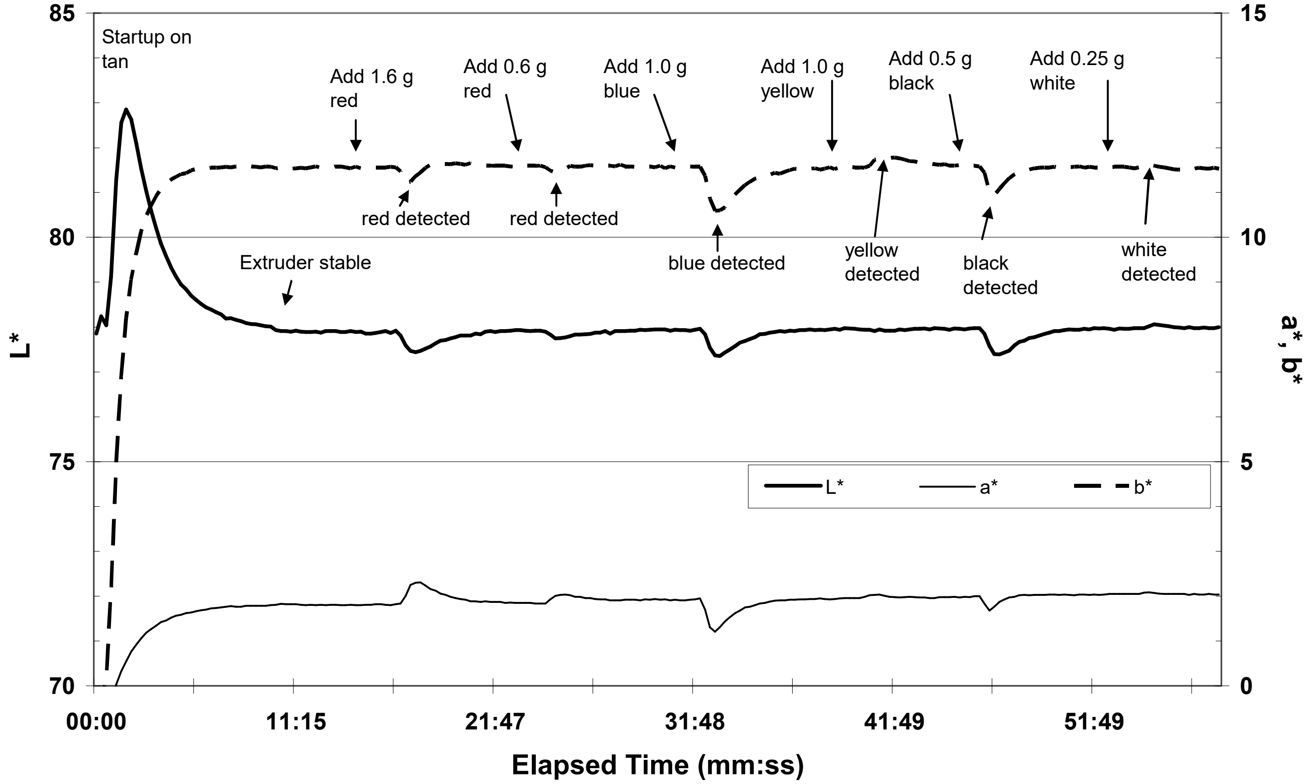

Figure 2. White polypropylene with two different product grades.

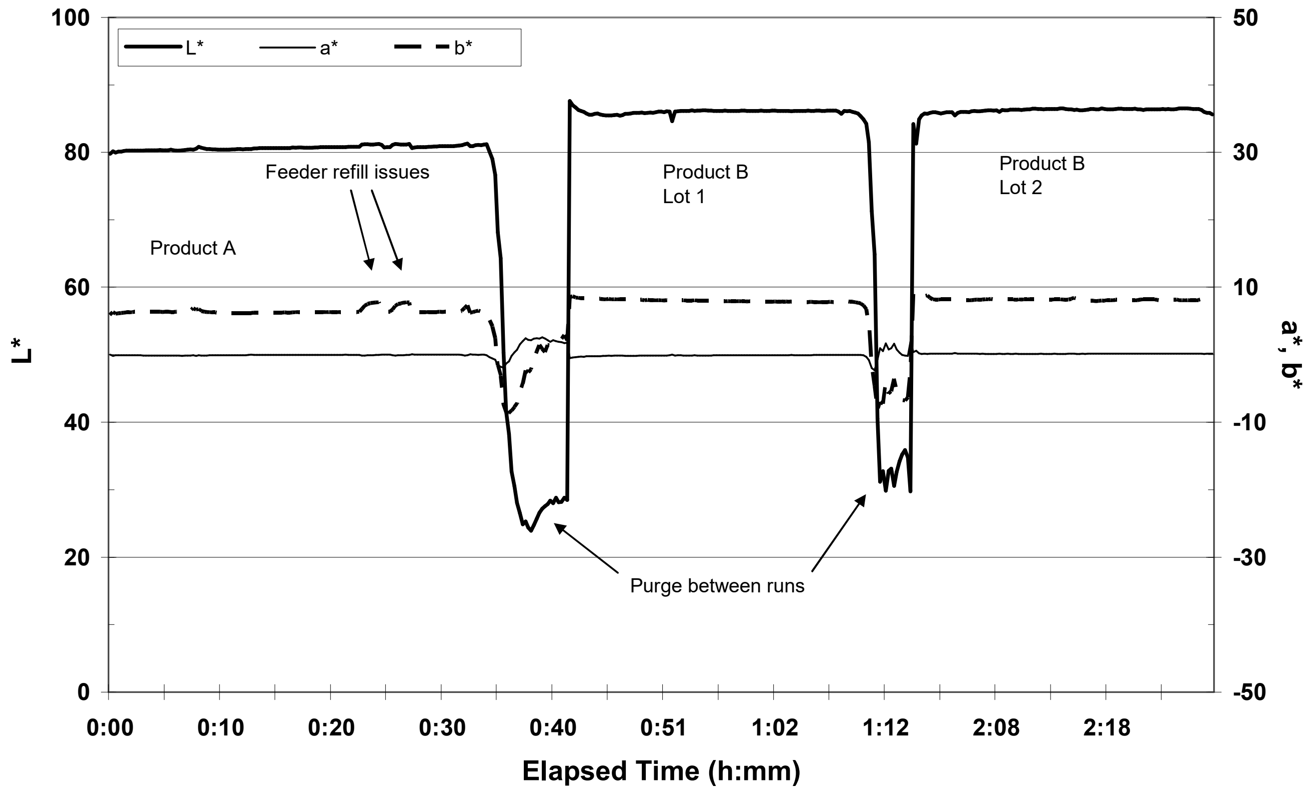

Figure 3. Effect of TiO_2 loading on L*

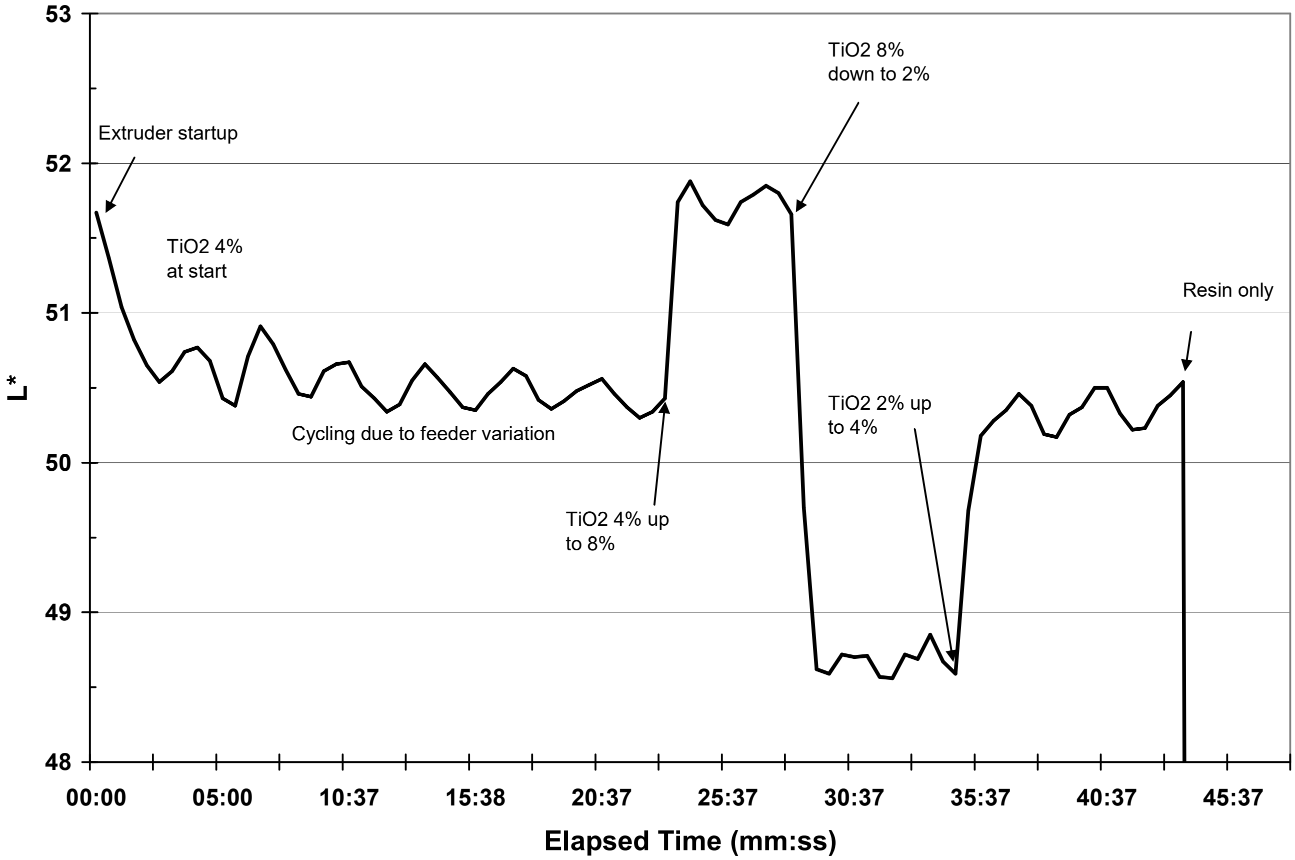

Figure 4. Production of gray PET from recycled materials.

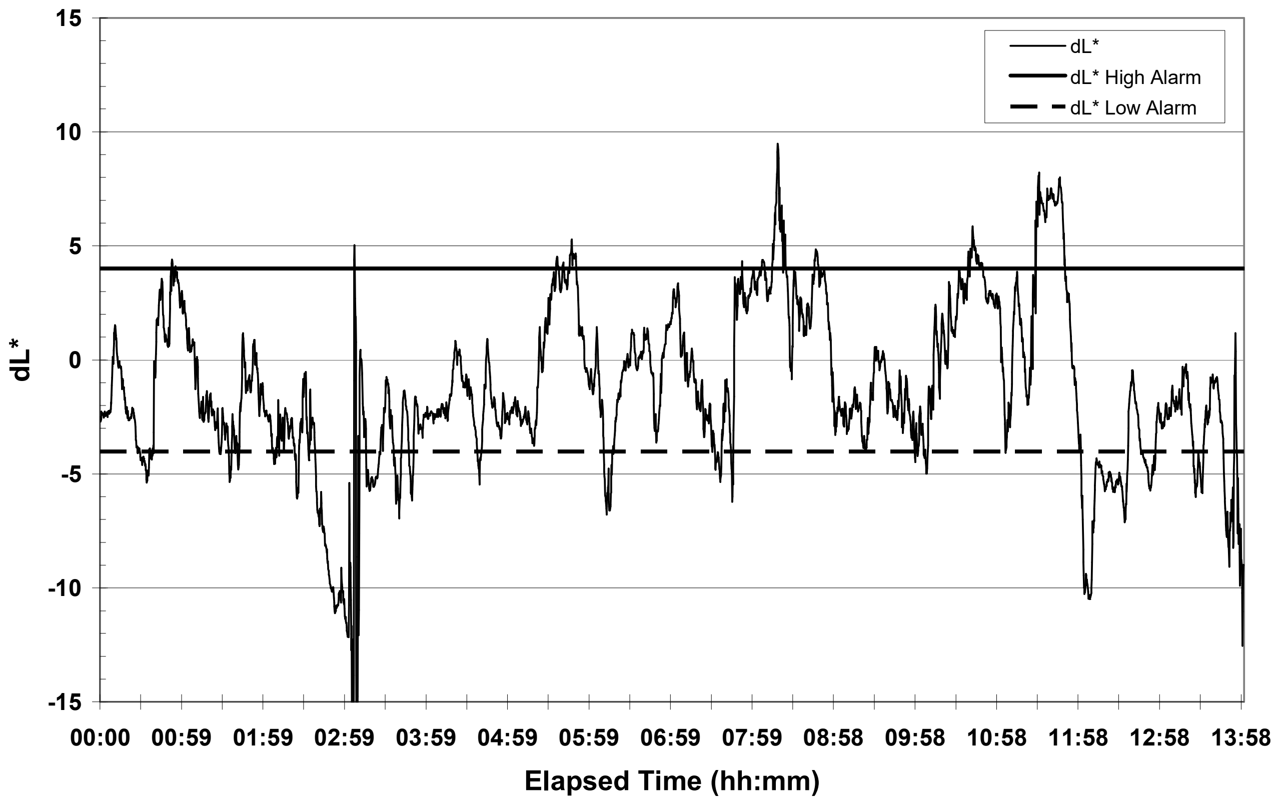

Figure 5. Injection molded PET pre-forms.

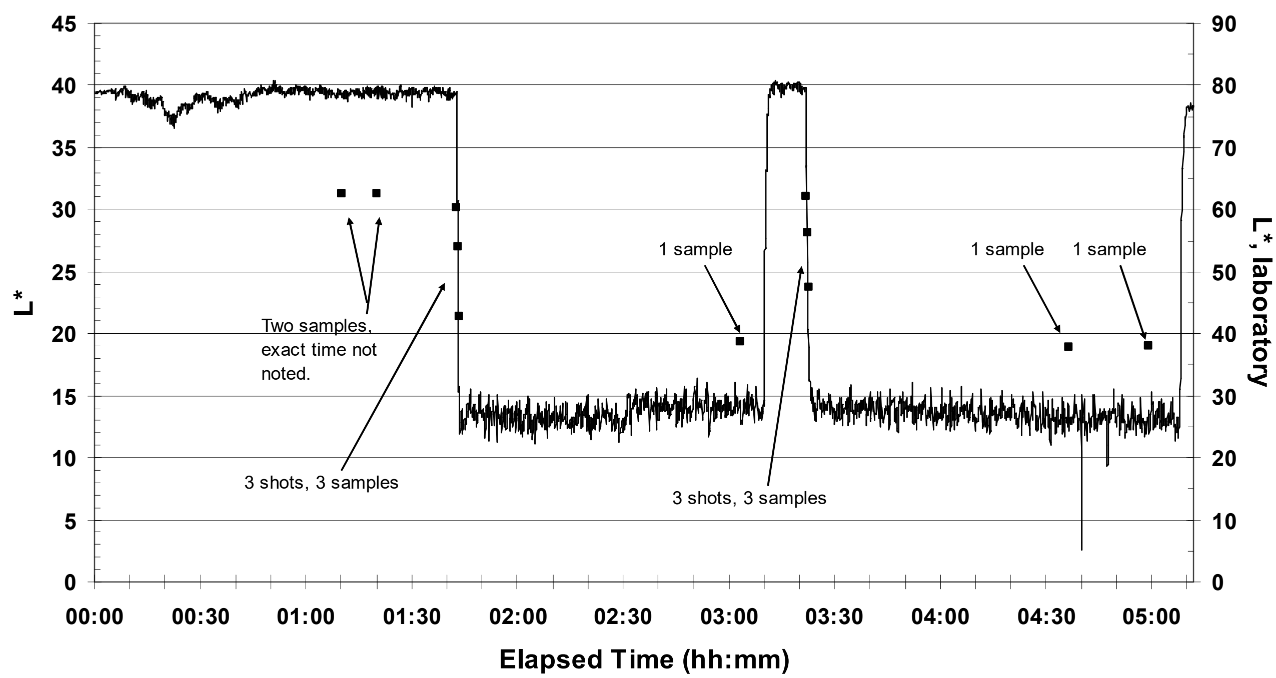

Figure 6. Effect of addition of black to polystyrene.

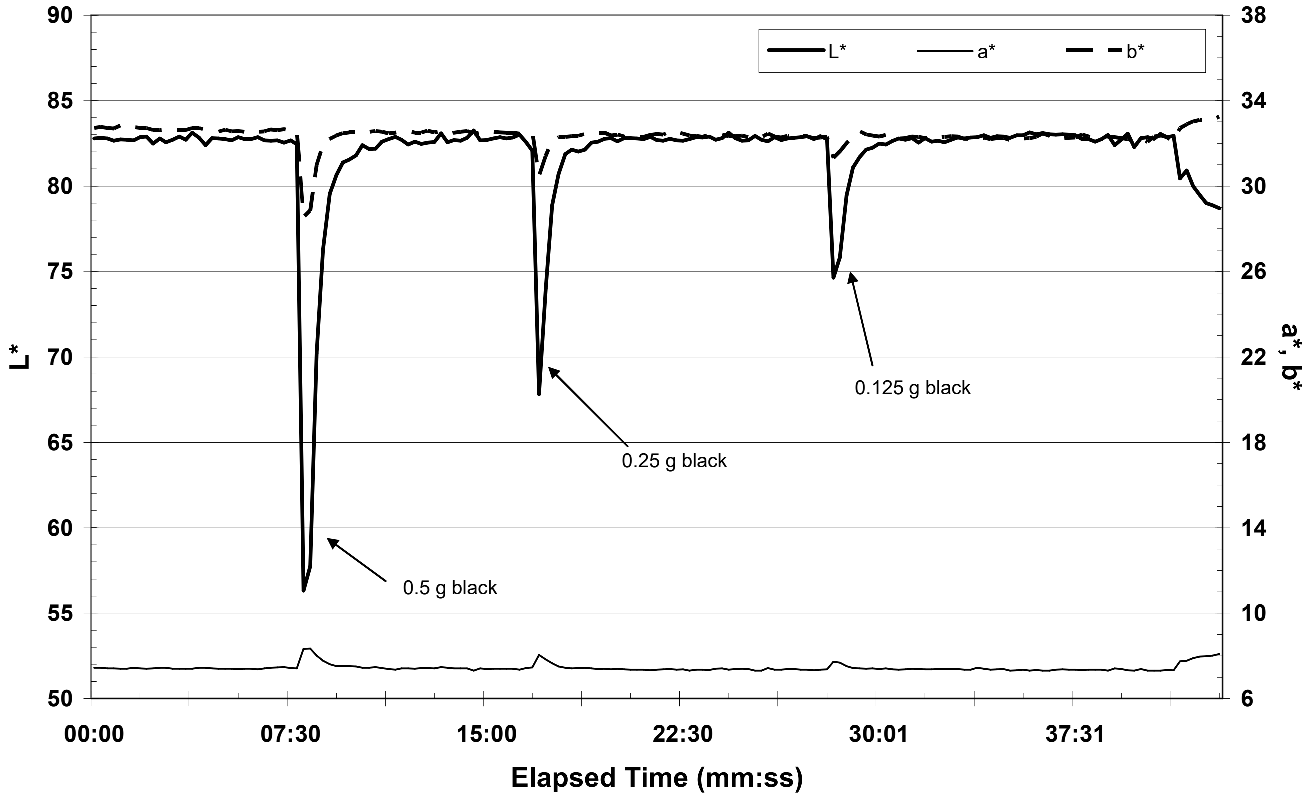

Figure 7. Online b* and laboratory b* for PET.

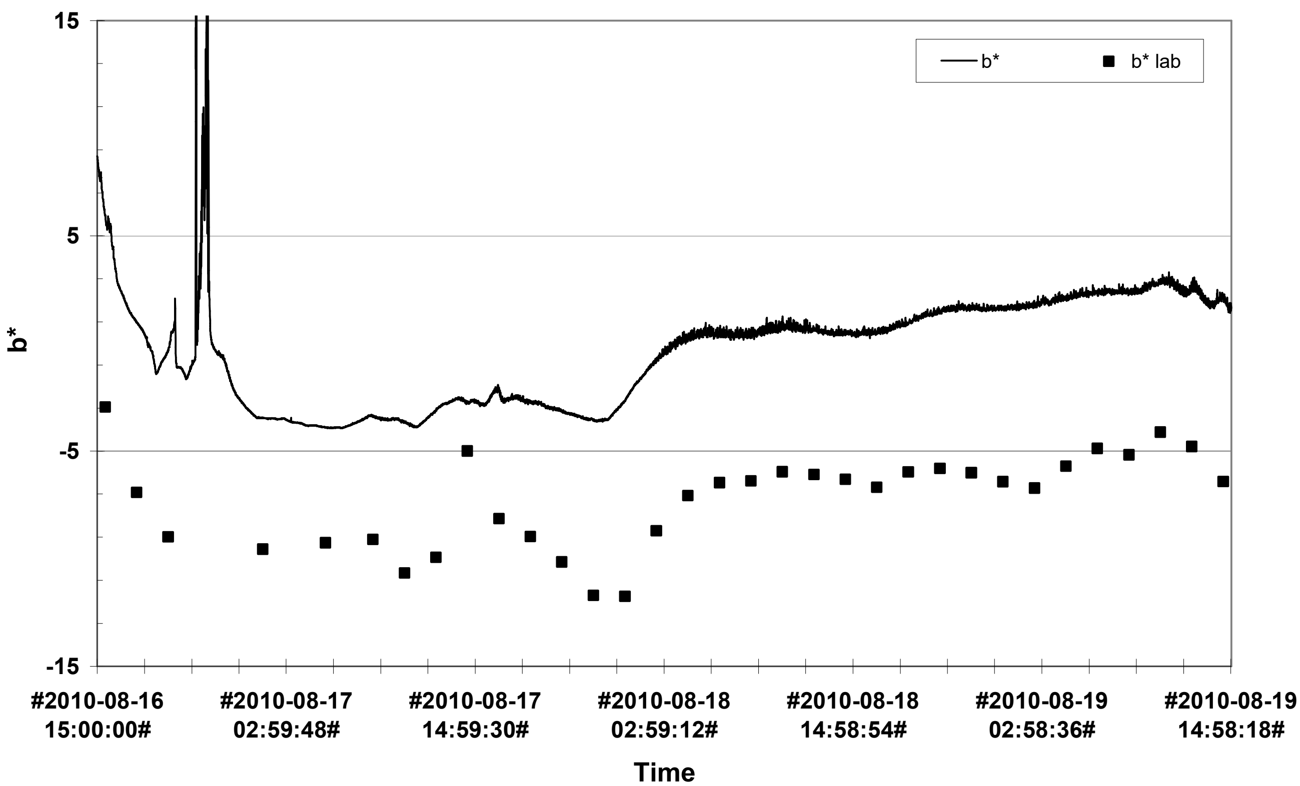

Figure 8. Correlation between online and laboratory b*