Quantitative analysis of tint in polymer pellets and disks

Application Note

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Introduction

The natural color (usually yellow) of many polymers such as acrylic, polycarbonate, and styrene–acrylonitrile (SAN) is unattractive for commercial purposes. Therefore, manufacturers add tint, or a dye to the polymer to mask the natural color. The final color and clarity of the polymer can determine the commercial value of the final product.

Traditional measurements of tint concentration require molding polymer pellets into disks. The color of the disks is then measured in a spectrophotometer or colorimeter. The time required to melt a representative sample of pellets, mold the melt into a disk, followed by a cooling down period can be one to two hours.

A fast and convenient method for quantitating the amount of tint directly in polymer pellets and molded disks is described.

This method could prevent the production of large amounts of incorrectly dyed polymer by detecting any problems quickly, allowing corrective action to be taken.

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Equipment

- DMS 300 UV–Visible Spectrophotometer
- Diffuse Reflectance Accessory (Integrating Sphere)
- Sekonic Printer/Plotter
- Concentration Application Module

Procedure

Note: Because of the nature of the polymer samples described in this paper, the name of the manufacturer, the polymer, the tint and wavelengths used, must remain proprietary.

Note: This method can also be performed with a Cary 1,3,4 or 5 instrument, fitted with a Diffuse Reflectance accessory and a Concentration application.

A Diffuse Reflectance Accessory (DRA) was used to measure both pellets and molded disks. The DRA consists of a 73 mm diameter integrating sphere with a built-in photomultiplier detector. The sphere's internal surface is coated with a white diffusing material - barium sulfate. The sphere can measure either diffuse reflectance (Figure 1A) or scattered transmittance (Figure 1B) where I_R and I_S represent reflected and scattered radiation, respectively. The sphere was chosen for this work because of its ability to collect a high percentage of the light scattered by the polymer pellets. The samples themselves were translucent, irregular-shaped spheroids of approximately 5 mm in diameter.

As single pellets were too small for representative absorbance measurements, a 1 cm square cuvette was chosen to hold a volume of pellets. Due to their irregular shape and size the pellets did not pack perfectly. Therefore, scattering of the incident radiation was observed when light from a spectrophot-ometer was passed through a cuvette of polymer pellets.
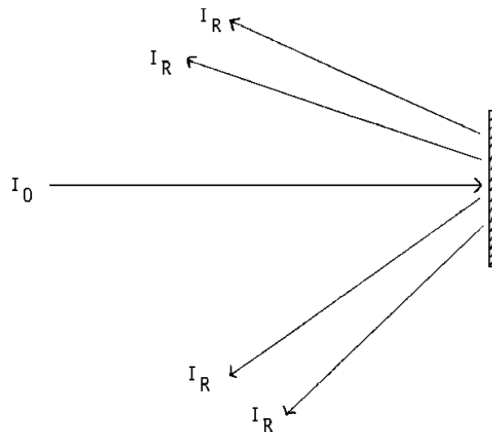

Figure 1A. Reflection off a sample surface.
I_R represents the reflected radiation,
I_0 represents the incident beam

This effect is illustrated in Figure 1B where I_0 is the incident radiation and is the scattered radiation. In a normal spectrophotometer arrangement the detector may be some distance from the cuvette. The light collection efficiency of such a system is thus very low. When the detector is much closer to the scattering matrix a much greater proportion of scattered radiation is collected. The integrating sphere acts as a highly efficient collector of scattered radiation. The sphere can be used in this manner if the cuvette containing the pellets is located so as to be part of the wall of the sphere as in Figure 2A. Therefore, all of the scattered radiation which passes through the rear face of the cuvette is collected by the sphere. Figure 2B illustrates the relationship between collection efficiency and distance between the sample and detector.

Once the integrating sphere is installed it can also be used to measure the absorbance of molded polymer disks. Molded disks are approximately 120 mm in diameter and 1/8" thick. The molded disks were measured by placing two disks back-to-back followed by a white reflectance disk. Light was passed through the two molded disks, reflected off the white disk, and passed back through the two molded disks into the sphere where it was detected. See Figure 3A.
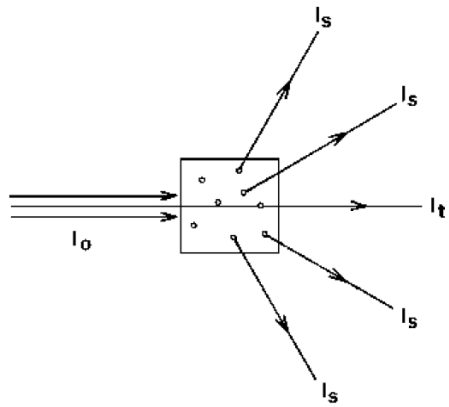
Figure 1B. Scattered transmittance of light through a turbid or opaque sample

I_0 represents the incident radiation

I_S represents the scattered transmittance

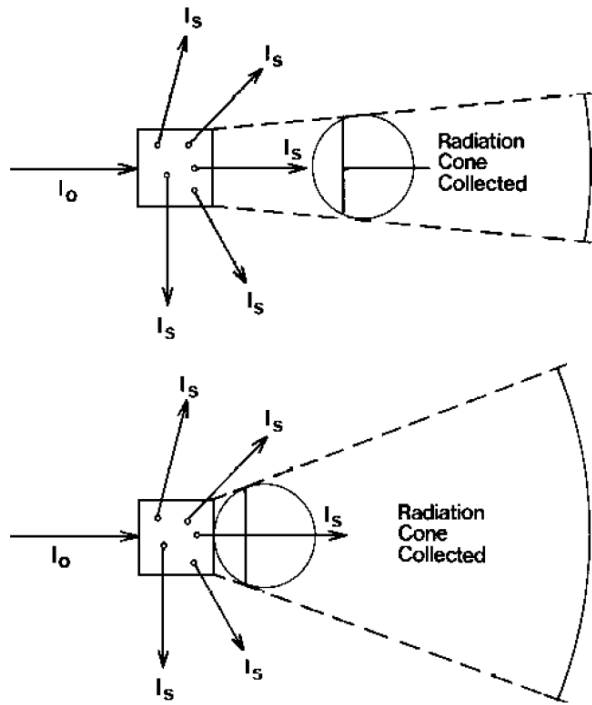I_t represents the transmitted light which has not been scattered

Figure 2A. The light collection efficency is increased by placing the sample so as to be part of the wall of the sphere
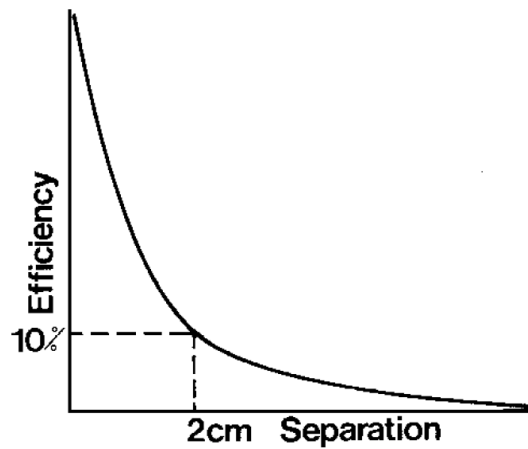

Figure 2B. The relationship between collection efficiency and the separation between the sample and the detector

Quantitative calculations were determined using a Concentration Application Module. The application module plugs into the back of the instrument and contains software for performing quantitative calculations. Access and interaction with the module is performed by following softkey instructions on the CRT of the instrument. Pellet and disk methods can be setup and stored in the module in non-volatile memory. Once a method is set up it can be recalled and executed automatically.
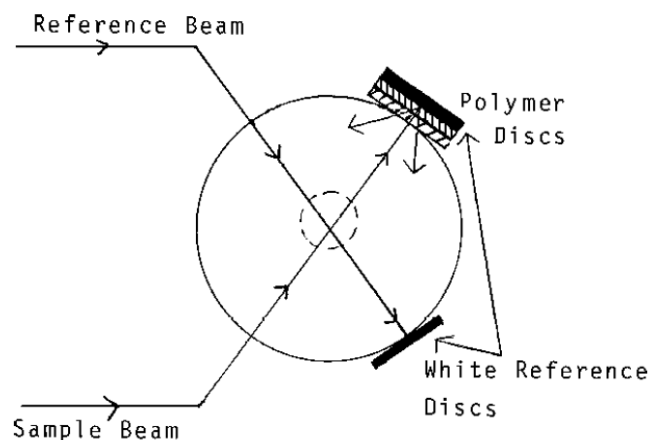

Figure 3A. The sphere configuration for the measurement of the molded polymer discs

Pellet analysis

The pellets were packed into a 1 cm square cuvette and placed in the light path before the sphere. See Figure 3B.

The concentration of tint in the polymer pellets was calculated by measuring the absorbance of the tint at its peak wavelength and a secondary wavelength. These wavelengths were chosen by utilizing a scanning UV–Visible spectrophotometer. The peak wavelength was determined by the spectrophoto-meter by scanning a sample of moderate concentration (ie. a sample containing enough tint to exhibit a well defined peak). A secondary wavelength was required because of the varying degrees of scattered radiation (or background) from sample to sample. The secondary wavelength was chosen from a series of scans as the wavelength where absorbance was independent of concentration of tint.

Since each pellet-filled cuvette will pack slightly differently, causing varying degrees of background scatter, the net sample absorbance was determined by subtracting the absorbance at the secondary wavelength from the absorbance at the peak wavelength. The sample net absorbance was then compared against a predetermined calibration curve stored in the Concentration Module. The Concentration Module automatically slews to each wavelength, performs the background correction, determines and then prints the final concentration. Five replicates on each sample can be determined in less than 3 minutes.
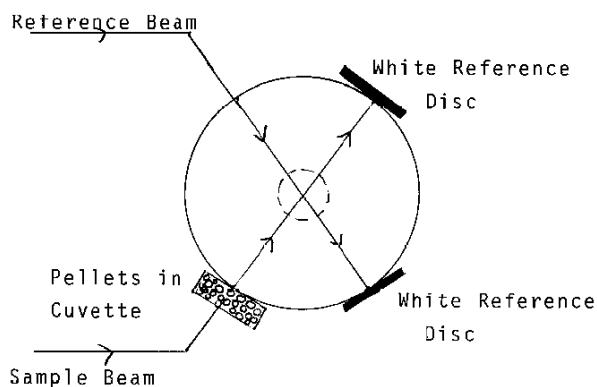

Figure 3B. The sphere configuration for the measurement of the polymer pellets

A calibration graph was determined by measuring, as described above, a series of polymer samples (or standards) of known dye content. Each standard was measured five times. Each measurement represented a different volume of pellets. The Concentration Module calculated the average of the five replicates and the final result was stored in memory. Because of the varying degrees of pellet size and homogeneity, five replicates were chosen to provide the best representative sample. Once the average standard values were determined the Concentration Module calculated a linear least squares calibration graph for the number of standards chosen. The calibration was stored in the Concentration Module in non-volatile memory. Subsequent samples were then measured as outlined previously, and their corresponding concentrations calculated from the calibration graph.

Molded disk analysis

The concentration calculations and calibration graph for tint in molded disks were determined as described in the pellet analysis section. Since disks do not exhibit scattering effects only one replicate was required.

Discussion

This method provides a fast, accurate way to quantitatively determine the concentration of tint in polymer pellets and disks. The calibration graph for pellets is shown in Figure 4 with a printout of the standard data and statistics indicated in Table 1.
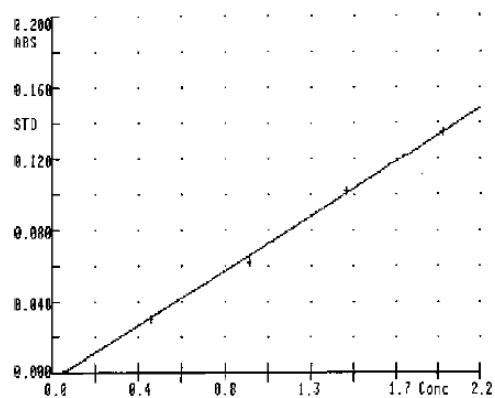

Figure 4. The calibration graph for the analysis of the dye content of the polymer pellets

Table 1. Standard data and statistics for the calibration graph in Figure 4

Standards	Factor 1.000	Nom Weight 1.000	WL Mode 2	WL1 xxx	WL2 xxx
	A 0.000	**B** 14.44	**C** 0.056	**Rsquared** 0.999	**Low** 0.000	**High** 2.000
	ABS	**CONC**			
1	-0.002	0.000			
2	0.030	0.500			
3	0.042	1.000			
4	0.101	1.500			
5	0.135	2.000			

Each concentration value is listed in parts per million (ppm) along with corresponding absorbance values. The correlation coefficient (the 'goodness' of the fit of the standard points) of 0.999 is excellent. The results of the same polymer pellets randomly remeasured as samples are shown in Table 2. The theoretical concentrations for each sample are listed in the last column.

Table 2. The results of the pellet samples analysis

Samples	Factor 1.000	Nom Weight 1.000	WL Mode 2	WL1 xxx	WL2 xxx
	A 0.000	**B** 14.44	**C** 0.056	**Rsquared** 0.999	**Low** 0.000	**High** 2.000
	ABS	**CONC**	**Weight**	**Theoretical Conc**	
1	0.135	2.006	1.000	2.0
2	0.033	0.536	1.000	0.5
3	0.098	1.476	1.000	1.5
4	0.069	1.055	1.000	1.0
5	−0.007	−0.039	1.000	0.0

The calibration graph for molded disks is indicated by Figure 5 with the printout of standard data and statistics shown in Table 3. The correlation coefficient for the disks' standard graph was 0.993.

(The results of the polymer disks randomly measured as samples are shown in Table 4.) Theoretical values are listed in the last column.
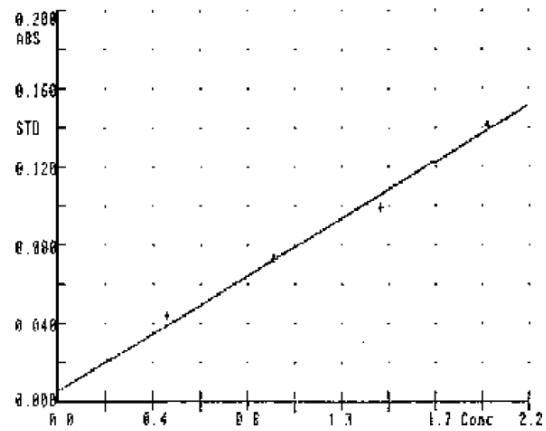

Figure 5. The calibration graph for the molded polymer discs

Table 3. Standard data and statistics for the calibration graph in Figure 5

Standards	Factor 1.000	Nom Weight 1.000	WL Mode 2	WL1 xxx	WL2 xxx
	A 0.000	**B** 15.03	**C** -0.079	**Rsquared** 0.993	**Low** 0.000	**High** 2.000
	ABS	**CONC**			
1	0.003	0.000			
2	0.044	0.500			
3	0.072	1.000			
4	0.099	1.500			
5	0.141	2.000			

Table 4. The results of the analysis of the molded polymer discs

Standards	Factor 1.000	Nom Weight 1.000	WL Mode 2	WL1 xxx	WL2 xxx
	A 0.000	**B** 15.03	**C** -0.079	**Rsquared** 0.993	**Low** 0.000	**High** 2.000
	ABS	**CONC**	**Weight**	**Theoretical Conc**	
1	0.094	1.301	0.000	1.5
2	0.069	0.952	0.000	1.0
3	0.142	2.056	0.000	2.0
4	0.038	0.497	0.000	0.5
5	0.004	−0.011	0.000	0.0

Additional applications

Another application of this technique uses the ability to perform wavelength scans on pellets and disks. This application offers the capability to fingerprint the tint used by various competitive manufacturers. Figure 6 shows wavelength scans of various polymer samples with different tints. UV–Visible wavelength scans also allow screening for possible contaminants.
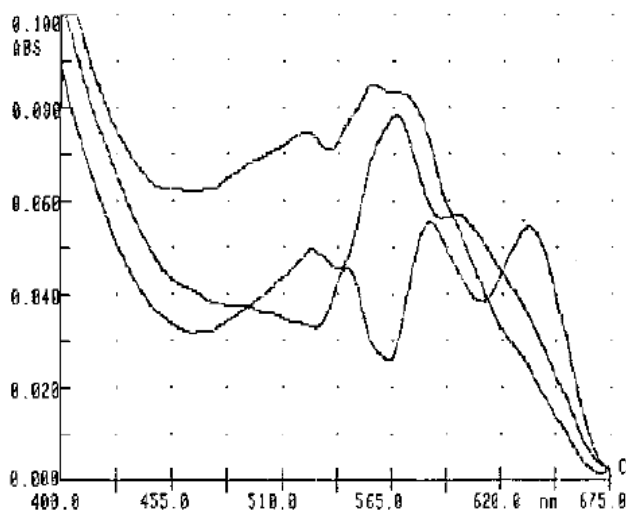

Figure 6. Wavelength scans of various polymer samples with different tints

Conclusion

The DMS 300 in conjunction with the Diffuse Reflectance Accessory and Concentration Application Module performs an automated analysis of polymer tint in pellets and disks. The analysis of tint in a polymer pellet sample can be accomplished in a matter of a few minutes, versus one to two hours by traditional methods. Potentially this can avoid large wastage of polymer material.

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