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Technical Paper

Pigment Influences on the Properties of Highly Filled Resin Systems

Abstract

The solubility, CIELAB color, matrix viscosity, air release and leveling properties of highly filled unsaturated polyester matrices made with different forms of Titanium dioxide colorant will be evaluated. A comparison of dry Titanium dioxide and color dispersions of TiO2 in various dispersion vehicles will be studied. With the advent of automated casting machines, there is an increased demand for liquid color dispersions. Liquid color dispersions can produce benefits when used in batch matrix processes. Dispersions can reduce mixing time, improve uniformity of color, reduce matrix viscosity, assist air release, improve flow and leveling, and decrease resin demand. The degree of whiteness, as measured by CIELAB, is generally considered to be a function of pigment concentration. This isn't always true, not all Titanium dioxide yields the same color at the same concentration and liquid color dispersions vary in their influence on matrix properties. Whiteness, air release, flow and leveling, matrix viscosity and cure properties may vary with various dispersions and dry pigments. A novel dispersion that reduces mixing time, improves flow and leveling, aides air release and reduces matrix viscosity will be presented along with the comparison data of the matrix properties using different color vehicles.

Introduction

While there are many specialty colors used in polyester composites, the mostly widely used color by far is white. To make these composites white, dry Titanium dioxide is added to the composite matrix or Titanium dioxide is milled into a "resin" to make a liquid Titanium dioxide dispersion to be added. To achieve a consistent color in the part, dry Titanium dioxide is usually first dispersed into the resin being used to make the part, the two methods of pigment addition can yield differences in process time, consistency, matrix viscosity, flow and leveling, and cure time.

Among composite manufacturers, particularly when making non-reinforced composites such as cultured marble, solid surface, centrifugal casting and "polymer concrete", there is a growing demand for managing quality, color consistency and cost through the use of automated metering and dispensing equipment. With resin heater options on this equipment, filler content can be taken to higher levels (75-88%) than has traditionally been possible. Because the amount of Titanium dioxide being introduced into the composite matrix is typically less than 2% by weight, liquid pigment dispersions can be more accurately charged through automated equipment using metering pumps than by metering in dry powder Titanium dioxide. With the advent of this equipment, there has been an increase in demand for liquid pigment dispersions.

Some of the differences and similarities in the properties of manufacturing composites using dry Titanium dioxides versus liquid dispersions are to be reviewed in this paper. The pigment type added can influence the solubility, color uniformity, CIELAB color, matrix viscosity, air release, flow and leveling and cure properties of the composite matrix. The type and particle size of the Titanium dioxide and the chemistry of the "resin" the pigment is dispersed in can impact these properties. For the purposes of this paper, the "resins" used to make these Titanium dioxide dispersions are monomer-free unsaturated polyesters.

These dispersions are typically 20-35% resin and 65-80% Titanium dioxide with viscosity ranges from 2000 – 8000 cps.

There are many variables that influence color and other properties of the composite. Many composite manufacturers perceive the color consistency of their composite is a result of the liquid resin color. Good manufacturing practices do result in consistent liquid color, but it is the cured resin color, (as measured by CIEL*a*b* or similar method, see Fig.1) that determines the appearance and pigment demand for the composite. The higher the L* value, the brighter the composite, the closer to zero a* (red-green) value and b* (blue-yellow) values are, the more neutral the color. From this data, the Delta E (total color difference) from the desired color or theoretical "brightest" can be calculated (ASTM D2244).

Filler colors do vary greatly, but Titanium dioxide is very efficient at normalizing the color of a composite at relatively low doses. In Fig.2, the color variability of five types of Aluminum trihydrate and four types of calcium carbonate typically used in highly filled (60-80% filler by weight) composites was evaluated. The L*, a*, b* values were identified with each filler both with and without pigment. Figure 2 demonstrates the variability in filler contribution to composite color and the normalizing effect of the pigment. The color differences in the unpigmented composites vary significantly more than the pigmented composites (a delta E of less than 1.0 is considered indistinguishable to the naked eye).

Solubility influences mixing process time, color consistency and cure consistency. Matrix viscosity and thixotropy influence air release, flow and leveling and uniformity of the part. Air release is influenced not only by viscosity but also by other factors such as resin molecular weight, filler particle size distribution, moisture, and gel time. In the manufacture of highly filled composites, it is also useful to cut cross sections of the part for visual examination under a microscope or measure air by density per unit volume.

The intent of this paper is to point out that Titanium dioxide is not just a pigment to achieve aesthetic color. Various sources and vehicles of Titanium dioxide can influence many properties of composite manufacturing and can be optimized to a specific process.

Experimental

To make the composite test samples, standard orthophthalic unsaturated polyesters containing 29-31% styrene by weight were used. Within an individual experiment, the same resin, catalyst types, catalyst level, filler type and filler level was used.

The mixing protocol for the solubility testing (Fig. 3-6) was to first mix resin and catalyst for one minute. This allows the most uniform distribution of catalyst because resin and catalyst are similar in viscosity and specific gravity and minimizes the possibility of catalyst absorption by pigmentation or fillers. Next, the background pigment (dark blue) was added and mixed a fixed number of cycles until homogeneous. Then the calcium carbonate was added and mixed a fix number of cycles until the matrix was homogeneous. Finally, dry Titanium dioxide or liquid Titanium dioxide dispersion was added to the catalyzed, blue colored matrix and mixed the specified number of cycles, then immediately cast into the mold and allowed to gel and cure. Each sample represents a different specimen, dry and dispersed, mixed for a specified number of cycles in a planetary mixer by the same process. Solubility, which influences the process time, color consistency and cureconsistency, was compared by visual examination and photographs.

The mixing protocol for the color testing (Fig. 7) was to first mix resin and catalyst for one minute. Next, the dry pigment or liquid dispersion was added and mixed a fixed number of cycles until homogeneous. Then the calcium carbonate was added and mixed a fix number of cycles until the mix was homogeneous. Finally, each sample was cast into the mold, and allowed to gel and cure overnight. The following day, the CIEL*a*b* color values were read on a Data Color CS-5 spectrophotometer (ASTM E308). Color values were reported for the L* value (dark-light), a* value (green-red) and b* value (blue-yellow) using the daylight light source (D65 10 deg). The color results reported in Fig. 2 were performed by the same procedure.

The mixing protocol for the viscosity testing was to mix resin and pigment only for one minute. This allowed more uniform dispersion of the dry pigment and takes advantage of the solubility of the dispersion in the resin due to similar viscosities. Then the calcium carbonate filler was added and mixed until homogeneous. The number of mixing cycles required for the matrix with the highest filler content (highest viscosity) was determined first then the same number of mixing cycles was employed with each subsequent sample. In the experiment with Filler X (Fig. 8), a blend of calcium carbonate and lightweight, the matrix viscosity was measured by a Brookfield HB viscometer (ASTM D2196), using a T-C spindle at 2.5 rpm and 25 degrees C (77 F). In the subsequent experiment, using Filler Y (Fig. 9), a straight calcium carbonate, Brookfield RV viscosities were run using spindle #2 @ 2 and 20 rpm. This provides data on the thixotropic index between the dry and dispersed pigment at various levels of filler. Viscosity and thixotropy values are significant because of their impact on air release and flow and leveling properties.

Air release is influenced by many factors: viscosity and thixotropy of the matrix resin, molecular weight, filler particles size distribution, moisture, and gel time. Of these, viscosity is the starting point to achieve proper air release. Composite manufacturers often wish to use the maximum amount of filler possible that achieves the desired properties. For the purpose of this paper, air release or air content in the composite was not measured, but can be viewed in the photos (Fig 3-6) used to illustrate the solubility of the pigments and time-lapse photos (Fig 10-13) of the flow and leveling.

The ability of the material to flow across the mold and fill the mold uniformly is a primary contributor to the strength, cosmetics and process cycle time of making the composite. Flow and leveling is evaluated by using a glass plate inclined between 30 and 45 degrees. To this plate is applied an equal mass of dry and dispersed TiO2 formulations of the same diameter and thickness. Visual observations and timed photographs can be used to capture their ability to flow; level and release entrained air (Fig. 10-13).

Results and Discussion

The difference in the solubility of dry Titanium dioxide pigment as compared to a liquid Titanium dioxide dispersion is represented in Fig. 3-6. In Figure 4, after 180 cycles under moderate intensity mixing, the liquid pigment is sufficiently dispersed that in a manufacturing operation, the composite matrix could be poured into the mold. The dry Titanium dioxide sample still contains some dry pigment at 360 cycles and even after 720 cycles there was one visible spec of undispersed pigment. It should be noted that undispersed pigment creates an uncured area in a composite, if Titanium dioxide is used to brighten an already low color filler such as ATH, this could be difficult to identify.

A common source of dry Titanium dioxide used in the composite industry was chosen for comparison to two different liquid dispersions. These dispersions were made using this same dry Titanium dioxide, the difference being the chemistry of the “resin” the Titanium dioxide was dispersed in. Dispersion A is a widely sold Titanium dioxide dispersion with a twelve-year performance history. Dispersion B was a newer product being evaluated for use in very highly filled composites made with automated mixing and dispensing equipment. In the test, the same amount of dry titanium and dispersion was used, therefore each dispersion sample contained 70% by weight as much Titanium dioxide as the dry sample. Fig. 7 demonstrates that the results were less than 0.17 delta E, meaning the difference was barely perceptible to the spectrophotometer and could not be perceived by the naked eye.

Another critical area for comparison was matrix viscosity. For the experiment represented by Fig. 8, in addition to the dry and dispersed pigments evaluated in the solubility experiment, an additional source of Titanium dioxide (“Dry C”) was added to the test. “Dry C” is an “equivalent” to “Dry B” that was reported to have the same general particle size distribution, oil absorption, and color. The filler used in Figure 8, is a blend of calcium carbonate and lightweight. These fillers tend to form very high matrix viscosities. The top table is a comparison at 75% filler, 25% resin and 1.4 pph pigment. At this dosing, both dispersed pigments result in lower viscosity than the dry pigment samples. The mix made with “Dry C” is much higher in viscosity than the other three. Reducing the filler to 71.5%, the results show that the matrix made with “Dry B” is lower in viscosity than the matrix made with the two dispersions, and again “Dry C” is significantly higher in viscosity.

Another series of tests was performed to compare the viscosity and thixotropy of matrix made with dry and liquid pigments. This is represented in Fig. 9. Samples were created using 78%, 75% and 70% straight calcium carbonate. The first observation is that in all cases, regardless of filler concentration and whether the viscosity is being measured at a high shear rate (20-rpm) or a low shear rate (2-rpm) the matrices made with dispersed pigment is lower in viscosity. The results indicate that all matrices are in fact thixotropic, but as you reduce filler (78%-70%) the thixotropic index drops (2.4 to 1.5).

The final test was to compare flow properties of the dispersions made from Dry B and Dispersed B. Equal formulations were made and poured on glass plates positioned at approximately 35 degrees from horizontal. A photo was taken when the material was first poured (Fig. 10). Photos (Fig. 11-13) were made every five minutes until the matrix actually gelled on the glass. The matrix made with the liquid dispersion is more highly elongated than the matrix made from the dry TiO2, indicating more linear flow. What was also observed in real time but is difficult to see from the photographs is that as each matrix releases air, the dispersed matrix exhibits smaller divots that tend to fill themselves as each bubble burst. This phenomenon occurred more slowly with the dry pigment.

Conclusions

There is a significant difference in the solubility of liquid dispersions in highly filled composites. This makes dispersions ideal for use in automated mixing and dispensing equipment where mixing time is minimal but can also be advantageous when batch mixing if process time is important. Due to “wet” nature of liquid pigment dispersions, an equivalent dose by weight of dispersion, containing 20-30% less TiO2 can yield the same color with some highly filled composites. The working viscosity of a highly filled matrix can be very susceptible to pigment type; various sources of Titanium dioxide can yield vastly different viscosities. Liquid dispersions can reduce matrix viscosity, especially when the filler loading exceeds 75%. The "resin" the pigment is dispersed in can also influence the rheology of the matrix. Different liquid color dispersions yield different viscosity, air release, flow and leveling properties. Dispersion A resulted in higher viscosity matrix than Dispersion B, and when compared in flow tests (not shown) performed more like the dry Titanium dioxide dispersion. Several tests have been presented that would allow a composite manufacturer to optimize their process for the parameters (such as cycle time, color, consistency) that they wish to control. Most importantly, the Titanium dioxide used to make composites is not a commodity. Through experimentation and product design it can be used to influence many properties that impact the appearance and performance of the composite.

Figure 1

L* a* b* Color Scale

- L* + Light
  Dark
- a* + Red
  Green
- b* + Yellow
  Blue

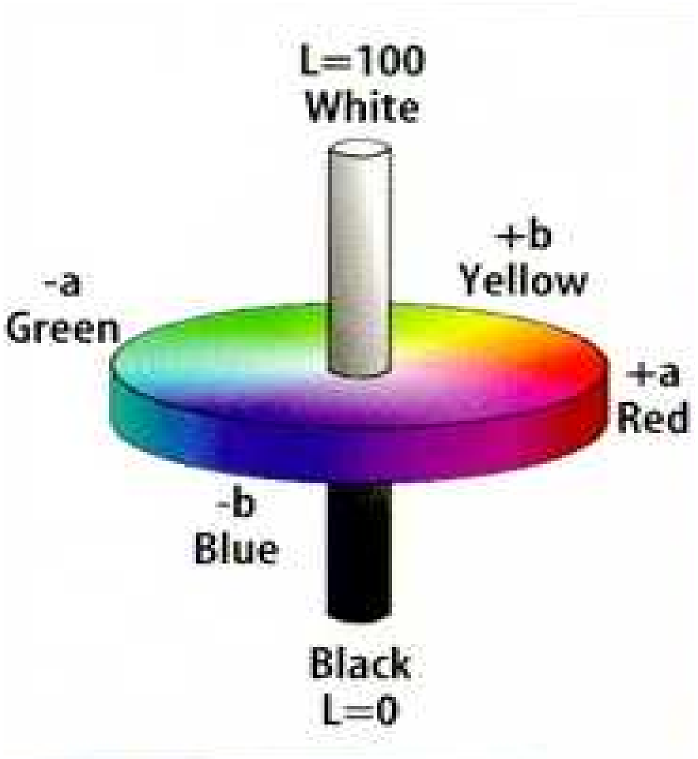

Figure 2

ATH	**FILLER ONLY:**				**@1.00% TiO2**			
	L*	**a***	**b***	**Delta E**	**L***	**a***	**b***	**Delta E**
ATH "A"	82.93	-0.23	4.41	**STD**	95.52	-0.78	2.16	**STD**
ATH "B"	76.87	-1.01	5.55	6.22	94.84	-1.13	2.98	1.12
ATH " C"	76.16	-0.91	5.81	6.95	94.81	-1.06	2.51	0.84
ATH "D"	75.97	-1.59	6.14	7.3	95.17	-1.18	2.79	0.82
ATH " E"	77.69	-1.24	4.17	5.34	94.14	-1.19	2.87	1.61
average	77.92	-0.996	5.216	**6.45**	94.9	-1.07	2.66	**1.10**

Calcium Carbonate	**FILLER ONLY:**				**@1.00% TiO2**			
	L*	**a***	**b***	**Delta E**	**L***	**a***	**b***	**Delta E**
CaCO3 "A"	85.48	-0.71	6.27	**STD**	94.56	-0.79	3.09	**STD**
CaCO3 "B"	81.09	-0.42	7.04	4.47	92.86	-0.68	2.51	1.80
CaCO3 "C"	81.49	-0.31	5.83	4.03	92.78	-0.71	3.07	1.78
CaCO3 "D"	82.56	-0.26	4.71	3.34	93.39	-0.77	2.65	1.25
average	82.66	-0.43	5.96	**3.95**	93.40	-0.74	2.83	**1.61**

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average	82.66	-0.43	5.96	**3.95**	93.40	-0.74	2.83	**1.61**

Figure 3

Dispersed and Dry: Comparison after 90 cycles

- 90 Mixing Cycles Completed
- Dry Titanium Dioxide specks (left side) are visible
- Paste Titanium Dioxide (right side) has “swirled” appearance

Dispersed and Dry: Comparison after 180 cycles

- 180 Mixing Cycles Completed
- Dry Titanium Dioxide specks (left side) are still visible
- Paste Titanium Dioxide (right side) closer to uniform appearance

Dispersed and Dry: Comparison after 360 cycles

- 360 Mixing Cycles Completed
- Dry Titanium Dioxide specks (left side) are still visible
- Paste Titanium Dioxide (right side) is uniform in appearance

Dispersed and Dry: Comparison after 720 cycles

- 720 Mixing Cycles Completed
- One Dry Titanium Dioxide speck (left side) can be seen
- Paste Titanium Dioxide (right side) is uniform in appearance

Figure 7-

Color Comparison of Dry and Dispersed Ti02@1.4pph

	L*	a *	b *	Delta E
Dry TIO2	93.84	-0.33	2.52	0
Dispersion A	93.84	-0.32	2.53	0.01
Dispersion B	93.71	-0.28	2.42	0.17

Figure 8-

TiO2 Viscosity Comparison @ 75% Filler X

Sample	Resin	Filler X	Pigment	Viscosity, cps
Dry C	150	450	8.4	2624000
Dry B	150	450	8.4	2080000
Disp A	150	450	8.4	1720000
Disp B	150	450	8.4	1696000

TiO2 Viscosity Comparison @ 71.5% Filler X

Sample	Resin	Filler X	Pigment	Viscosity, cps
Dry C	171	429	8.4	736000
Dry B	171	429	8.4	556800
Disp A	171	429	8.4	640000
Disp B	171	429	8.4	619200

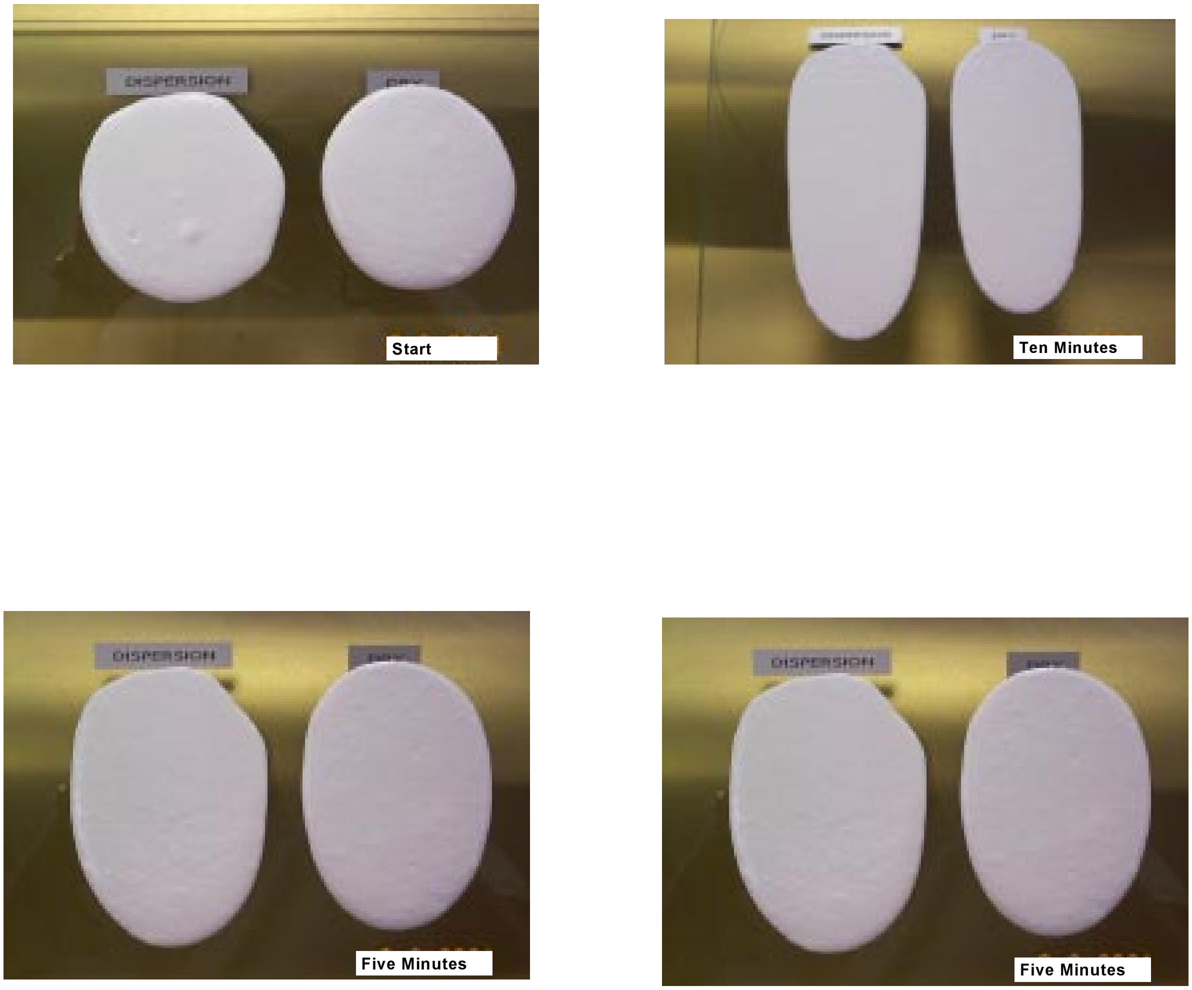
Figure 9

Viscosities of Dry TiO2 B and Dispersed TiO2 B in Filler Y

Sample	Resin	Filler Y	Dry TiO2	Viscosity S.D @2rpm's	Viscosity S.D @20rpm's	Thix Index
DRY B	110	390	7.5	3330000	1390000	2.4
DRY B	125	375	7.5	1230000	604000	2.04
DRY B	150	350	7.5	410000	282000	1.45

Sample	Resin	Filler	Dispersed TiO2	Viscosity S.D @2rpm's	Viscosity S.D @20rpm's	Thix Index
Disp B	110	390	7.5	2150000	886000	2.43
Disp B	125	375	7.5	1020000	492000	2.07

Figure 10


DISPERSION
DRY
Start
Ten Minutes
Five Minutes
Five Minutes