Pursuing Partial TiO_2 Independence in Low-Density Polyethylene Masterbatch and Compound

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Abstract

One of the most widely used industrial minerals today is titanium dioxide (TiO_2), which primarily delivers superior whiteness and opacity to consumer and industrial products. Challenges in using titanium dioxide are well known and include volatility in price and supply due to producers' inability to effectively manage fluctuating demand. As a result, market dynamics warrant exploration of alternative products for high-volume applications – such as plastics.

One innovative alternative that is rapidly gaining traction is engineered cristobalite, a mineral product that offers its users some level of titanium dioxide independence alongside additional "enhancements" not possible with titanium dioxide alone. This paper highlights the benefits of incorporating cristobalite into plastics, with a focus on processing, mechanical strength, weathering, color and opacity. The analysis suggests that between 25% and 50% of TiO_2 can be replaced in plastic compound by a particular type of cristobalite (PIGMENT E) without any depreciation of aesthetic or performance attributes.

Introduction: The Value of Partial Titanium Dioxide Independence

Over the last decade, global supply chains for key ingredients have become strained by competing tariffs, recurring virus outbreaks and war. As a result, despite the existence of multi-billion-dollar manufacturers, the supply of titanium dioxide (TiO_2) has been markedly volatile and uncertain.

For businesses that have to purchase TiO_2 in North America, it has been challenging to manage fluctuating pricing dynamics. More specifically, in 2021 and 2022, prices spiked to all-time highs for most markets, followed by nine subsequent month-over-month price declines. While these events have recently precipitated somewhat of a "buyers' market," experts do not expect this drop in price to continue; supply volatility will set the stage for increased pricing into 2024 and beyond.

For starters, the limited availability of high-quality sources of ore dictates that the variable costs for TiO_2 production will not see any downward pressure moving forward. Furthermore, due to the complexity of the TiO_2 production process, there are regulatory hurdles, raw material challenges, and significant capital investments necessary to increase production capacity. This means that new supply is unlikely to come online in either Europe or North America in the foreseeable future.

To address the challenges of sourcing titanium dioxide, companies with reformulation capabilities have been actively reducing their dependence on titanium dioxide through the adoption of alternative white pigments. These new products offer relief by replacing a portion of titanium dioxide. Substitutions of just 10% to 25% result in hundreds of thousands to millions of dollars' worth of savings for adopters, and of course, limit reliance on a difficult-to-source material.

A recently launched mineral pigment product based on cristobalite silica technology is steadily gaining market acceptance in thermoplastics. In contrast to TiO_2, it has a more favorable set of manufacturing requirements, including: more stable supply directly from North American mining assets, a robust process for production that is independent of bulk commodity chemicals, and easily scalable production to accommodate increases in demand. The following study details U.S. Silica's latest evaluation of EWP-5's performance in thermoplastics with a focus on its ability to replace up to 50% of titanium dioxide without adversely impacting color, opacity, weathering, mechanical strength, and processing.

A New Pigment for Consideration

Silicon dioxide, also known as silica, is an oxide of silicon with the chemical formula SiO_2, commonly found in nature as quartz. In many parts of the world, silica is a major constituent of sand and is therefore extremely abundant. Cristobalite (/krɪˈstoʊbəˌlaɪt/) is a mineral polymorph of silica that is formed at very high temperatures. It has the same chemical formula as quartz, SiO_2, but a distinct crystal structure which, when ground to the micron-scale, yields a product with outstanding whiteness and hardness, similar to that of the very well-known white pigment, titanium dioxide (TiO2). While finely-ground cristobalite certainly requires a sophisticated manufacturing process, it is a more cost-effective and less resource-intensive method than conventional titanium dioxide manufacturing, and thus, the market price for cristobalite is less than that of TiO_2.

U.S. Silica has recently commercialized a cristobalite material, EverWhite Pigment 5 (EWP-5), which will be referred to in the remainder of this paper as “PIGMENT E”. Due to its intrinsic properties, it is well-equipped to replace appreciable portions of TiO_2 in plastic compound formulations. Per Table 1 below, the small particle size (D-90 of 5.8 microns, D-50 of 2.4 microns), high whiteness (L* of >98.0), and impressive Mohs hardness of 6-7 make Pigment E a compelling offset candidate for TiO_2. The refractive index of EWP-5 is less than that of TiO_2. However, when used for replacing around 50% of TiO_2, its small particle size coupled with a proprietary particle morphology produce an effective opacity that is greater than expected in plastics. These “first principles” of Pigment E warrant further investigation into how much TiO_2 can be replaced without a negative impact on critical aesthetic characteristics such as opacity and color.

Table 1: “PIGMENT E” Fundamental Properties

TYPICAL PARTICLE SIZE (LASER DIFFRACTION)		TYPICAL MEASURED PROPERTIES	
D-90 (µm)	5.8	Hunter L	> 98.0
D-50 (µm)	2.4	a	0.7
D-10 (µm)	1.3	b	1.0
GENERAL PROPERTIES			
Mohs Hardness	6-7	Refractive Index	1.49
pH	9-10	Specific Gravity	2.33

Proof of Concept for Thermoplastics

To objectively verify the technical merits of replacing TiO_2 with PIGMENT E, a “ladder study” approach was taken. Considering the difference in refractive index, a straight 1:1 replacement by weight was ruled out and a maximum replacement level of 50% was selected for “proof of concept” work in both plastic masterbatch and compound formulations. As this was the first time that TiO_2 would be replaced by PIGMENT E, it was decided to include one additional replacement level of TiO_2, 25%, to build a baseline from which to optimize in the future. With performance and aesthetic data for 0%, 25%, and 50% replacements of TiO_2, the study aimed to give formulators an idea of conservative replacement levels for their applications.

Materials and Methods

Methods:

Formulation planning and testing was conducted by the Akron Rubber Development Lab, an independent testing laboratory specializing in rubber, plastic and latex with the following accreditations and registrations:

- A2LA ISO 17025:2017 accredited; ISO 9001:2015 registered; ISO 13485:2016 registered; FDA compliant

Two distinct sets of formulations were developed and then tested. The first was a proof-of-concept masterbatch formulation with a control loaded with 50% TiO_2, and the second was a proof-of-concept compound formulation with a control loaded with 9% TiO_2. Reformulation designs were built out as follows:

Table 2: Ladder Formulations – Proof-of-Concept Masterbatch:

Formulation Ingredient	Control	25% TiO_2 Rep.	50% TiO_2 Rep.
LDPE	50%	50%	50%
TiO_2	50%	37.5%	25%
PIGMENT E	0	12.5%	25%
Irganox 1010	0.5%	0.5%	0.5%

Table 3: Ladder Formulations – Proof-of-Concept Compound:

Formulation Ingredient	Control White	25% TiO2 Rep.	50% TiO2 Rep.	100% TiO2 Rep.
LDPE	90%	90%	90%	90%
TiO2	9.0%	6.8%	4.5%	0.0%
PIGMENT E	0.0%	2.3%	4.5%	8.9%
Irganox 1010	1%	1%	1%	1%

Each batch of materials was mixed in a 1.6-liter BR Banbury and sheeted out on a two-roll mill. Materials were weighted and mixed per ASTM D3182 specifications and then mixed per the following protocol:

Single Pass Mix	
0:00 time point	LDPE, ½ TiO2 or PIGMENT E
2:00 time point	Add the rest of the TiO2 or PIGMENT E
At 240 F	Sweep
At 260 F	Sweep
At 280 F	Drop

Masterbatch and compound was next used to make injection-molded LDPE plaques, which were then further evaluated per the standards below. Plaques were roughly 1/8th of an inch thick.

Evaluation of the three proof-of-concept **masterbatch** formulations was carried out via ASTM/ISO methods as follows:

- Melt Flow Rate of Plastics – ISO 1133-1
- Tensile Properties of Hard Plastics - ASTM D638
- Calculation of Color Differences – ASTM D2244

Further evaluation of the four proof-of-concept **compound** formulations was carried out via ASTM/SAE methods as follows:

- Tensile Properties of Hard Plastics – ASTM D638
- Gardner Impact Resistance – ASTM D5420
- Calculation of Color Differences – ASTM D2244
- Density – ASTM D792

- Accelerated Weathering via Xenon Arc – SAE J2527
- Visual Opacity Assessment and Opacity Over Paper Backing - TAPPI T425

Materials

- LDPE: Certene LDF-0221 with Melt Flow Rate (190°C, 2.16kg measured by ASTM D1238) of 2.0 g/10 min
- TiO_2: Kronos 2211, a rutile, Type II (per ASTM D 476) pigment produced by the chloride production process with a TiO_2 content of greater than 95.5% and density of 4.1 g/cm^3
- PIGMENT E: Cristobalite SiO_2 material from U.S. Silica with a D90 particle size of less than 5.8 microns and density of 2.33 g/cm^3
- Process Aid: Irganox 1010

Results and Discussion: Proof-of-Concept White Masterbatch

Work with the "Proof-of-Concept Masterbatch" was completed first, and thus, the processing and quality evaluation data from those formulations will be shared prior to the "Proof-of-concept Compound" data.

Mixing of the masterbatch was done with a 1.6-liter BR Banbury and started at 50 RPM with a fill factor of 74%. The Banbury was heated with oil to 121 C (250 F) before adding the plastic and filler materials. Mixing time, max temperature, average power (HP), integrated power (HP*min) and MFI (Melt Flow Index) per ISO 1133-1 were recorded and are reported in Table 4 below.

Table 4: Processing Characteristics of Masterbatch

Batch	Time (min)	Max Temp. (°C)	Power (HP)	Speed (RPM)	AVG Power (HP)	Integrated Power (HP*min)	MFI (2.16 kg/10 min at 190 ℃)
Control	4.82	147.93	5.23	102.66	5.23	27.62	0.221
25% TiO_2 Rep.	5.42	149.30	5.26	98.49	5.24	26.18	0.169
50% TiO_2 Rep.	4.75	149.22	5.52	98.32	5.52	23.04	0.145

Only minor differences were observed in mixing parameters, processing energy, and MFI when replacing up to 50% of TiO2 content with PIGMENT E. This suggests that no changes in processing equipment or parameters would be required when formulating with the PIGMENT E material as a replacement for TiO2.

For understanding changes in mechanical strength, tensile testing (per ASTM D638) performance of the samples is shown in Table 5 and Table 6 below and in the subsequent figures (Figures 1-4).

Table 5: Measured Tensile Stress Values per ASTM D638 for Masterbatch

Sample	Mean Stress at Break (psi)	Mean Stress at Break (psi) - SD	Mean Stress at Yield (psi)	Mean Stress at Yield (psi) - SD
Control	2,161	68	2,226	81
25% TiO_2 Rep.	1,974	81	1,984	55
50% TiO_2 Rep.	1,924	66	1,979	68

Table 6: Measured Tensile Strain Values per ASTM D638 for Masterbatch

Sample	Mean Strain at Break (%)	Mean Strain at Break (%) - SD	Mean Strain at Yield (%)	Mean Strain at Yield (%) - SD
Control	67%	6%	64%	6%
25% TiO_2 Rep.	61%	4%	59%	4%

50% TiO_2 Rep.	56%	6%	53%	6%

Figures 1-4: Tensile Stress and Strain of Masterbatch Formulations

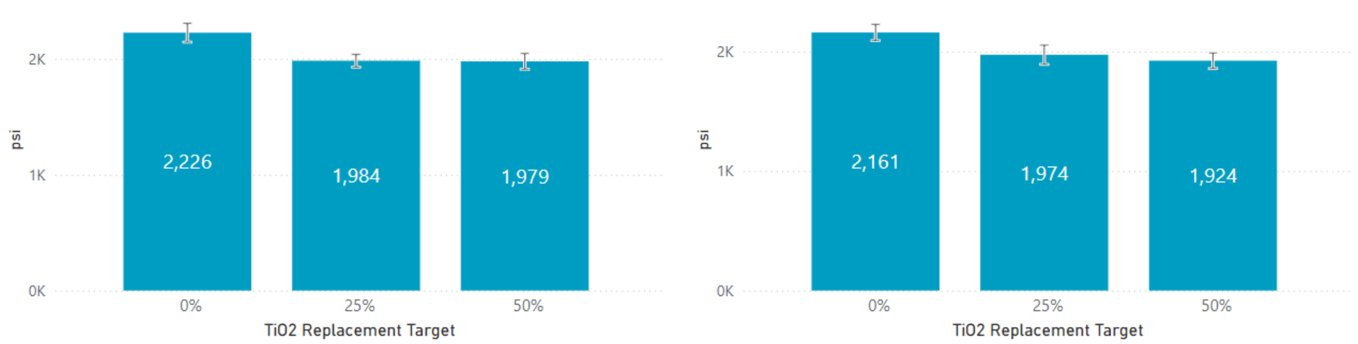
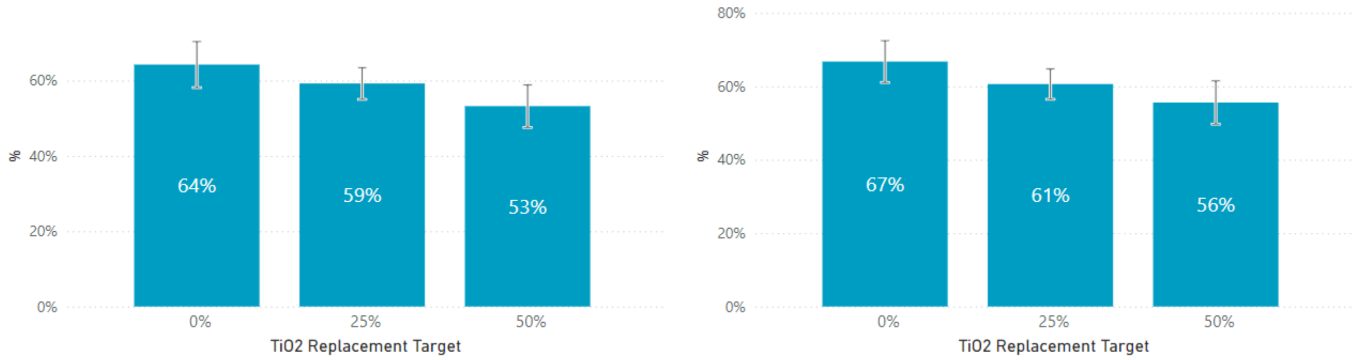


Figure 1: ASTM D638 - Mean Tensile Stress at Yield (psi)

Figure 2: ASTM D638 Mean Tensile Stress at Break (psi)

Figure 3: ASTM D638 Mean Tensile Strain at Yield (%)

Figure 4: ASTM D638 Mean Tensile Strain at Break (%)



Tensile testing shows no statistically significant differences in performance as more TiO_2 is replaced by PIGMENT E.

Analysis of color change was completed per ASTM D2244 with an X-Rite CI7600 color spectrophotometer with a D65 10º observer. Reported below are the Lab* color differences between samples.

Table 7: Color Shift upon Replacement of TiO_2 with Pigment E

Sample	DL*	Da	Db	Delta E
Control	-	-	-	-
25% replacement of TiO_2	- 0.41	0.15 R	0.34 Y	0.56
50% replacement of TiO_2	- 0.52	0.07 R	0.24 Y	0.58

The color analysis indicates only minor changes to the color-space achieved by samples with 25% and 50% replacement of TiO_2 by PIGMENT E in these highly loaded plastic formulations. While somewhat dependent on the color in question, in general, a Delta E value of 1.5 or less typically indicates a “color-match” for a majority of thermoplastics applications, and thus, samples formulated with the PIGMENT E material did not significantly change the color.

Results and Discussion: Proof-of-Concept White Compound

To verify that good performance can also be expected at lower pigment loading levels, a 9%-loaded white compound was evaluated next.

To begin, the density of each sample was assessed via a measurement of their specific gravity per ASTM D792. Table 8 below indicates the measured specific gravity for each formulation.

Table 8: Compound Ladder Formulations: Reduction of Titanium Dioxide (%)

Formulation Ingredient	Control White	25% TiO_2 Rep.	50% TiO_2 Rep.	100% TiO_2 Rep.
LDPE	90%	90%	90%	90%
TiO_2	9.0%	6.8%	4.5%	0.0%
PIGMENT E	0.0%	2.3%	4.5%	8.9%
Process Aid	1.0%	1.0%	1.0%	1.0%
Specific Gravity	0.987	0.985	0.979	0.972
% Change	-	-0.2%	-0.8%	-1.5%

As expected from the lower density of PIGMENT E (2.33 g/cm3) compared with TiO_2 (4.1 g/cm3), as greater quantities of TiO_2 are replaced by the PIGMENT E, the density of the compound made with these minerals decreases.

Again, to look for any changes in mechanical strength, summarized tensile testing (per ASTM D638) performance of compound samples is shown in Table 9 and Table 10 below and in the subsequent figures (Figures 5-8).

Table 9: Measured Tensile Stress Values per ASTM D638 for Compound

Sample	Mean Tensile Strain at Break (%)	Mean Tensile Strain at Break (%) - SD	Mean Tensile Strain at Yield (%)	Mean Tensile Strain at Yield (%) - SD
Control	255%	198%	18%	2.4%
25% TiO_2 Rep.	338%	146%	19%	2.6%
50% TiO_2 Rep.	391%	171%	21%	3.2%
100% TiO_2 Rep.	402%	84%	21%	2.6%

Table 10: Measured Tensile Strain Values per ASTM D638 for Compound

Sample	Mean Tensile Stress at Break (psi)	Mean Tensile Stress at Break (psi) - SD	Mean Tensile Stress at Yield (psi)	Mean Tensile Stress at Yield (psi) - SD
Control	1,479	331	1,430	32
25% TiO_2 Rep.	1,474	200	1,418	39
50% TiO_2 Rep.	1,640	N/A	1,430	22
100% TiO_2 Rep.	1,507	267	1,424	27

Figures 5-8: Tensile Stress and Strain of Compound Formulations

Figure 5: ASTM D638 - Mean Tensile Stress at Yield (psi)

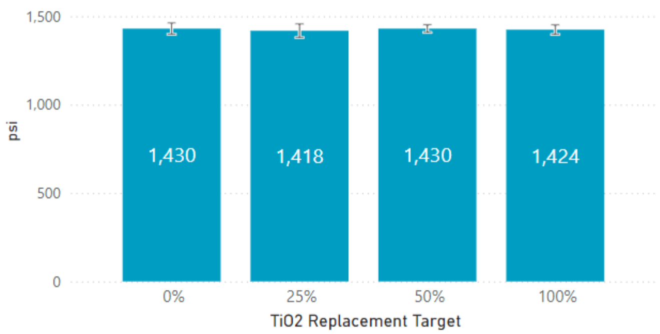


Figure 6: ASTM D638 Mean Tensile Stress at Break (psi)

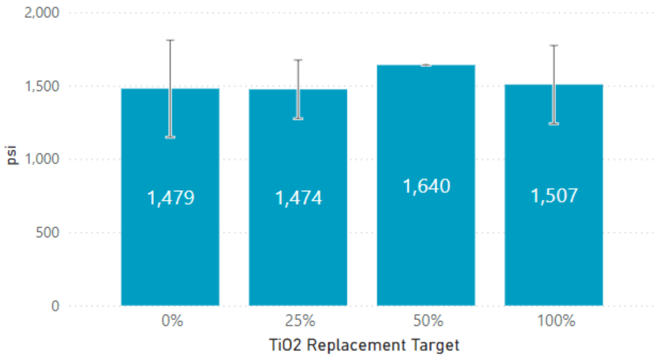


Figure 7: ASTM D638 Mean Tensile Strain at Yield (%)

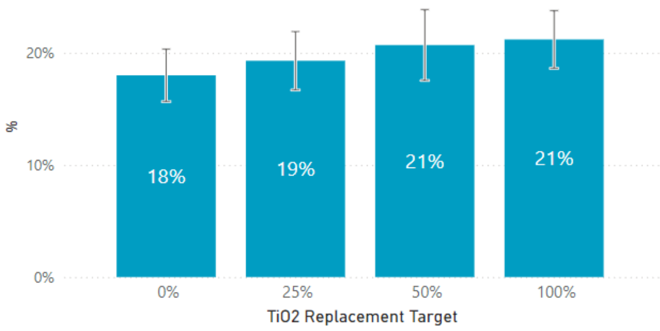
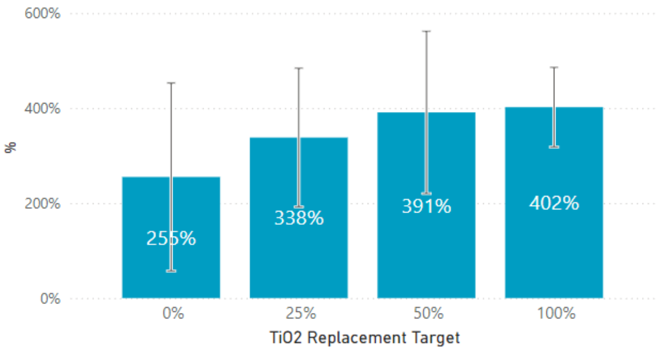


Figure 8: ASTM D638 Mean Tensile Strain at Break (%)



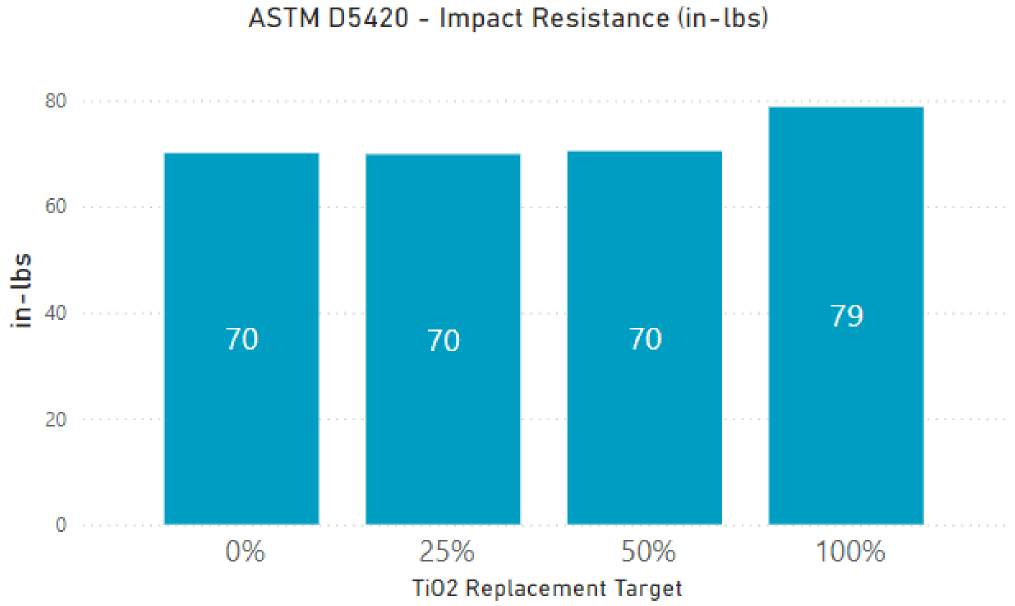
Tensile testing of the compound not only shows minimal differences in the stress at yield and at break, but also a potential upward trend in performance of strain at yield and at break as more TiO_2 is replaced by PIGMENT E. Per this data, nothing catastrophic is expected for compound product formulation and there may be an advantage to using PIGMENT E for mechanical strength in LDPE applications.

To take a broader view of mechanical strength performance, the team also evaluated Gardner Impact Resistance per ASTM D5420 in the compound samples. Results are shown in Table 11 and Figure 9 below.

Table 11: Measured Gardener Impact Resistance per ASTM D5420 for Compound

Sample	Thickness, (in.)	Gardner Impact (In-lbs.)	Type of Failures
Control	0.073	70.0	40% Cracks 60% Non-Failures
25% TiO_2 Rep.	0.069	69.8	45% Cracks 55% Non-Failures
50% TiO_2 Rep.	0.070	70.4	30% Cracks 20% Ductile 50 % Non-Failures
100% TiO_2 Rep.	0.071	78.7	35% Cracks 10% Ductile 55% Non-Failures

Figure 9: Measured Gardener Impact Resistance per ASTM D5420 for Compound Formulations



Impact resistance testing of the compound shows no difference when comparing the control sample versus 25% and 50% replacements, but surprisingly indicates a positive improvement in performance when 100% of TiO2 is replaced by PIGMENT E. Per this data, nothing catastrophic is expected for compound product formulation with PIGMENT E and there may be an advantage to the use of 100% PIGMENT E for impact resistance in LDPE applications.

An analysis of color change was completed per ASTM D2244 with an X-Rite CI7600 color spectrophotometer with a D65 10º observer. Reported below are the Lab* color differences between samples.

Table 12: Color Shift upon Replacement of TiO_2 with Pigment E

Sample	DL*	Da	Db	Delta E
Control	-	-	-	-
25% replacement of TiO_2	- 0.27	- 0.14 G	0.21 Y	0.37
50% replacement of TiO_2	- 1.40	- 0.24 G	0.35 Y	1.46
100% replacement of TiO_2	-14.52	- 1.42 G	- 1.71 B	14.69

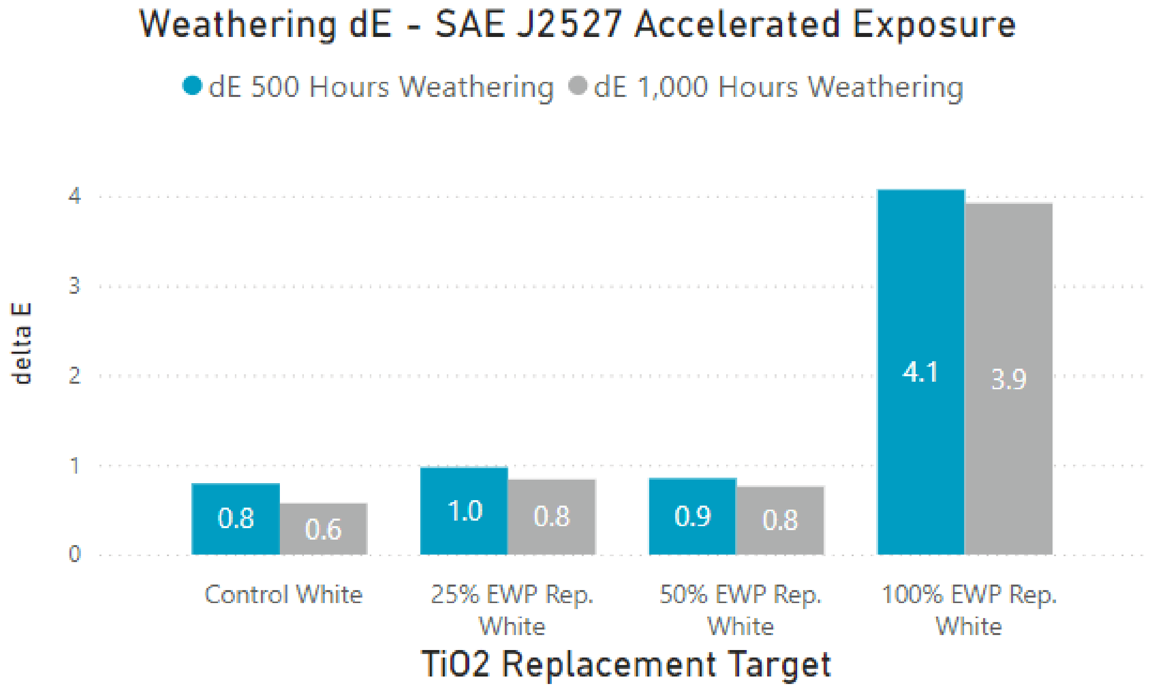
The color analysis indicates only minor changes to the color-space in samples with 25% and 50% replacement of TiO_2 by PIGMENT E in the compounded plastic formulations. A Delta-E value of less than 1.5 typically indicates a "color-match" for a significant portion of thermoplastics users and producers, and thus formulating with the PIGMENT E material is not causing an appreciable change in color. A greater difference is observable when 100% of the TiO_2 is replaced by PIGMENT E, in which case the Delta E is 14.69, due mostly to a decrease in L*, which is indicative of a darker sample and a decrease in opacity.

Next, per the SAE J2527 test protocol, an analysis of the dE after weathering was completed. Results are shown in Table 13 and Figure 10 below.

Table 13: ASTM D2244 Color Difference Data of Compound Samples Weathered via SAE J2527

500 Hours = 659.3 kJ/m^2		ΔL	Δa	Δb	ΔE	Averaged ΔE
Control White	Specimen 1	-0.04	-0.05	-0.88	0.88	0.79
	Specimen 2	-0.11	-0.05	-0.68	0.69	
25% TiO_2 Rep. White	Specimen 1	-0.05	0.00	-1.04	1.04	0.97
	Specimen 2	-0.07	0.01	-0.89	0.89	
50% TiO_2 Rep. White	Specimen 1	0.02	0.02	-1.01	1.01	0.85
	Specimen 2	-0.48	0.13	-0.47	0.69	
100% TiO_2 Rep. White	Specimen 1	-0.97	-0.48	3.73	3.88	4.07
	Specimen 2	-1.11	-0.34	4.09	4.25	
1000 Hours = 1318.7 kJ/m2		**ΔL**	**Δa**	**Δb**	**ΔE**	**Averaged ΔE**
Control White	Specimen 1	-0.13	-0.03	-0.62	0.63	0.57
	Specimen 2	-0.09	-0.01	-0.51	0.51	
25% TiO_2 Rep. White	Specimen 1	-0.01	0.02	-0.92	0.92	0.84
	Specimen 2	-0.09	0.04	-0.75	0.76	
50% TiO_2 Rep. White	Specimen 1	0.21	0.00	-0.99	1.01	0.76
	Specimen 2	-0.29	0.13	-0.38	0.50	
100% TiO_2 Rep. White	Specimen 1	-0.64	-0.47	3.50	3.59	3.92
	Specimen 2	-1.10	-0.34	4.09	4.25	

Figure 10: ASTM D2244 Color Difference Data of Compound Samples Weathered via SAE J2527



The weathering analysis indicates only minor differences in the color change after weathering observed in samples with 25% and 50% replacement of TiO_2 by PIGMENT E after 500 and 1,000 hours of accelerated weathering. Samples formulated with up to a 50% replacement of TiO_2 with PIGMENT E do not show an appreciable change in color over time in comparison to control samples with TiO_2 only. However, a much greater difference is observed when 100% of the TiO_2 is replaced by PIGMENT E, in which case the Delta E after 500 and 1,000 hours of weathering is 4.1 and 3.9, respectively. This is likely connected to the lower refractive index of PIGMENT E particles without any TiO_2 to form synergy with. This enables greater UV-light penetration into the polymer matrix and subsequent further degradation of the polymer, which aligns with the increase in b* (yellowing), typical of polymer degradation.

Finally, both subjective opacity differences and quantitative analyses of opacity were evaluated. Per the images below (Images 1-4), there is a minor change in the amount of light passing through plastics with small portions of their TiO2 replaced by PIGMENT E. However, when all TiO_2 is replaced, there is a significant loss of opacity. This suggests that for aesthetic purposes, less than 100% of the TiO_2 should be replaced. Quantitative measurement of light reflectance per the TAPPI T425 standard corroborates this suggestion (Figure 11).

Images 1-4: Subjective Opacity Analyses of Compound Formulations

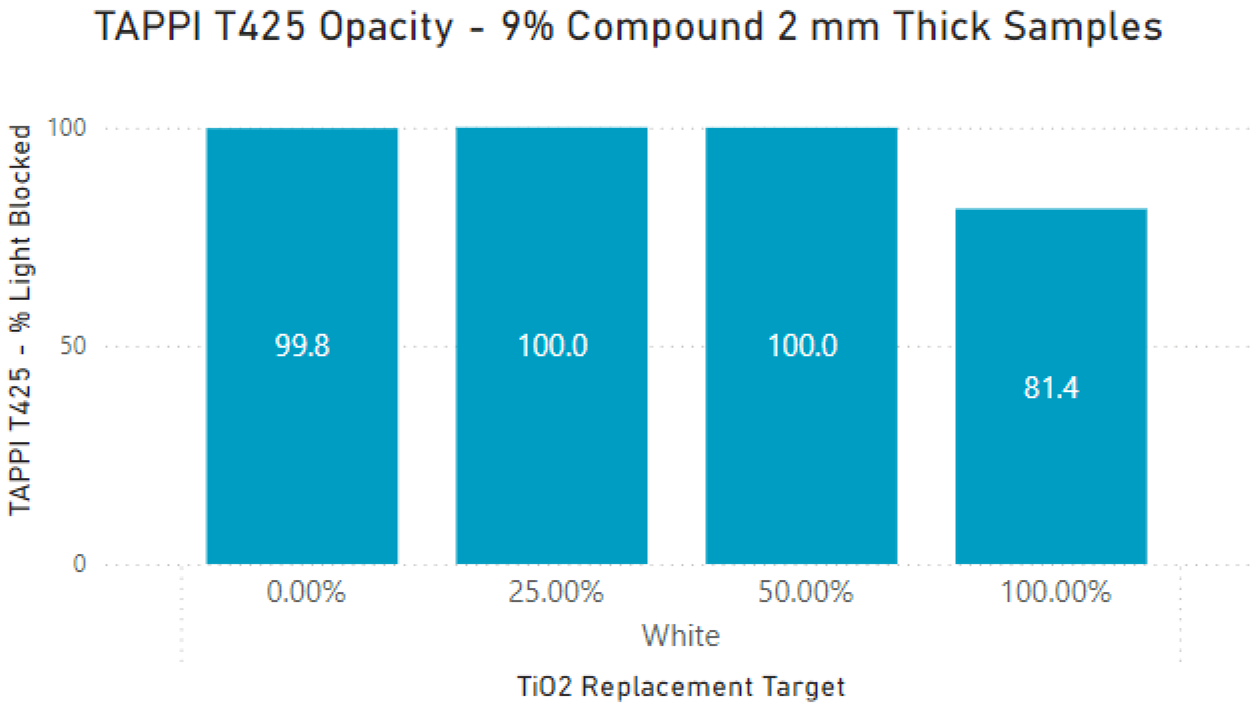
Image 1:
Control:
100% TiO$_2$
dE: N/A

Image 2:
25% Pigment E
Replacement
dE: 0.37

Image 3:
50% Pigment E
Replacement
dE: 1.46

Image 4:
100% Pigment E
Replacement
dE: 14.69

Figure 11: TAPPI T425 Opacity Measurement of 2 mm Injection Molded Samples



Conclusions

The combination of processing, mechanical, color, opacity and weathering data indicate that the cristobalite material PIGMENT E is an excellent candidate for replacing up to 50% of the TiO_2 in plastic compound formulations today. There may also be some mechanical strength advantages to consider when entirely replacing TiO_2 with PIGMENT E, particularly in non-exterior and non-aesthetic applications, but further exploration is likely necessary in that arena. With the nearly 50% difference in the cost of TiO_2 and PIGMENT E and thus far positive performance indications for masterbatch and compound made with PIGMENT E, this new silica-based material certainly warrants further study by relevant industry experts. A summary of the performance of PIGMENT E replacement samples in comparison with TiO_2 control samples is presented in in Table 14 below.

Table 14: Summary of Compound Formulation Performance

Sample	Processing	Mechanicals	Weathering	Opacity	Color	Cost
Control	✓	✓	✓	✓	✓	-
25% replacement of TiO_2	✓	✓	✓	✓	✓	+
50% replacement of TiO_2	✓	✓	✓	✓	✓	++
100% replacement of TiO_2	✓	+	-	-	-	+++