White Paper: PixClear® TiO_2 Titania Nanocomposite Materials for High-Refractive Index Films

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Abstract

In this white paper we present characterization data from films made with Pixelligent PixClear® anatase titanium dioxide (TiO_2) nanoparticles with mean particle diameters of 10 nm (PTPG-2) and 20 nm (LTPF-1) dispersed in a acrylate-based binder system with refractive index of 1.55. Variables within the films include TiO_2 weight loadings between 50 – 90% and film thicknesses between 1 – 3 microns. The films for both nanocrystal types demonstrate refractive index values as high as 1.88 and 1.96 at 589 nm, high transparency of between 50 – 90% in the visible light spectrum (400 – 700 nm), low haze, and minimal color increase (b*) as compared with comparable ZrO_2 films. There is a particle size dependence on film RI that favors a larger mean particle diameter.

Keywords: anatase, titanium dioxide, nanoparticle, nanocrystal, nanoimprint, ink jet, high refractive index, nanocomposites

Introduction

Titanium dioxide (TiO_2) is widely used in consumer products including coatings, plastics, paper, cosmetics, and food coloring. TiO_2 has a rutile stable phase in bulk and an anatase metastable phase in nano crystal form. The RI for the anatase phase is 2.56 at 589 nm [1]. On the 200-nm scale the high refractive index (RI) of TiO_2 creates highly reflective surfaces, and through scattering effects particles of this size create the highly desirable white color for that which titanium dioxide is known [2]. When the nanoparticles are less than 40 nm, however, they are much smaller than the wavelengths of visible light and there is minimal scattering.

Using these smaller TiO_2 nanoparticles, a combination of organic-inorganic nanocomposites can be made to produce clear dispersions and films. The combined functional and mechanical properties of these nanoparticles can add value in many engineering disciplines and applications. Organic polymer materials are beneficial for their low molecular weight, flexibility, and manufacturing processability. Inorganic materials, such as TiO_2, are desirable for their hardness, strength, and high RI values. Organic-inorganic nanocomposites can be made to have high RI values close to 2.0, while also being solution processable for use in commonly used manufacturing processes [2].

One of the leading potential applications of these TiO_2 nanoparticles is for use in Diffractive Optical Elements (DOE). DOE's are very small structure patterns used in optical devices to change the phase of the light propagated through the optical structures. The application ranges and markets served for DOE are very broad. Examples of DOE consist of diffractive optical waveguides, beam splitters and diffractive diffusers for optical sensors, medical laser treatments and diagnostics instruments, optical distance and speed measurement systems, fiber coupling, and laser display and illumination systems. The materials must be optically clear and nanoimprintable to meet industry needs in DOE applications [3] and balancing these optical and mechanical properties is vital for the growing demands in high RI DOEs.

One of the leading markets where DOE is having an impact is Extended Reality, which is expected to reach $18.8 billion (USD) in 2020 [4]. Balancing the optical and mechanical properties is critical to deliver the optically clear and nanoimprintable materials that this industry is demanding. Pixelligent's PixClear® TiO_2 technology enables TiO_2 nanocomposites for high-RI applications such as AR/VR where maintaining optical clarity and the necessary mechanical properties for nanoimprinting are as critical as high-RI values.

PixClear® TiO_2 Nanocrystals

PTPG-2

TiO_2 nanocrystals with an average core size of 5 nm as shown in Transmission Electron Microscopy (TEM) image 1a (inset image), are surface modified or capped with capping agents that make these nanocrystals compatible with various monomers and polymers including acrylates, epoxies, and siloxanes. The capping agents on PTPG-2 are designed for maximum compatibility without any functional groups that can crosslink with the polymer matrix. The capped nanocrystals form a uniform dispersion in propylene glycol monomethyl ether acetate (PGMEA) with a single narrow Dynamic Light Scattering (DLS) peak centered around 10 nm (Figure 1b).

LTPF-1

TiO_2 nanocrystals with an average core size of 15 nm as shown in TEM image 1b (inset image), are capped with capping agents that make these nanocrystals compatible with various monomers and polymers including acrylates, epoxies, and siloxanes. In addition, LTPF-1 nanocrystals are capped with functional capping agents that enable them to crosslink with acrylic/methacrylic monomers, reducing the need for a crosslinker and improving mechanical properties. These capped nanocrystals also form a uniform dispersion in PGMEA with a single narrow DLS peak centered around 20 nm (Figure 1d).

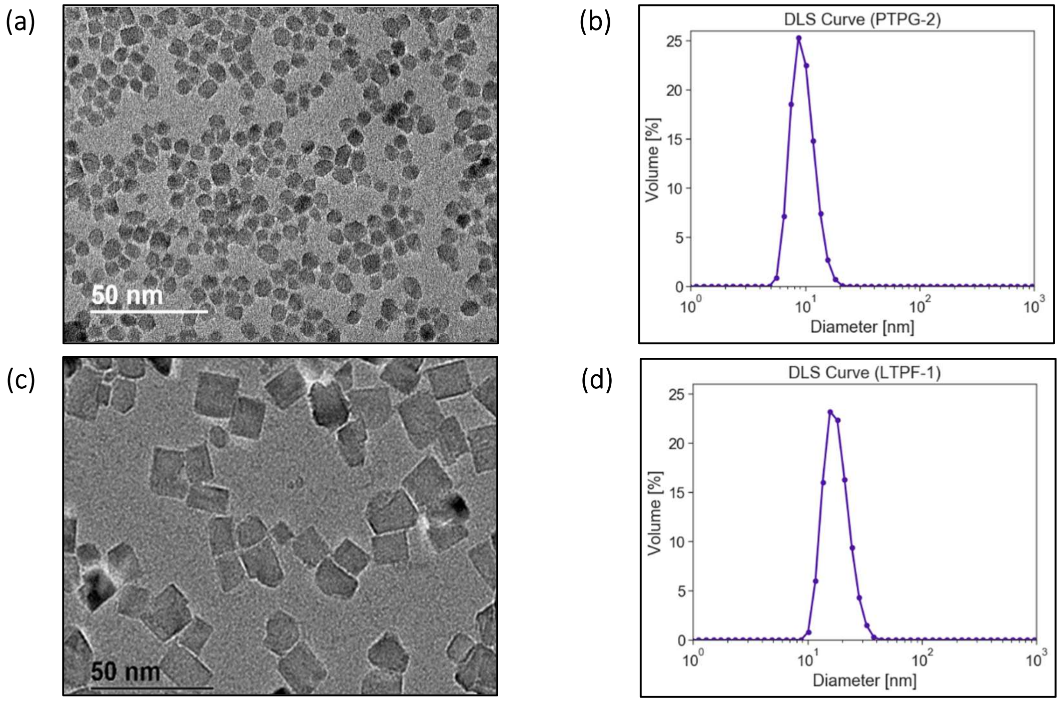

Figure 1. Core particle size of TiO_2 nanocrystals by TEM (a) PTPG-2 and (c) LTPF-1 and Particle size distribution curves for PTPG-2 (b) and LTPF-1 (d) TiO_2 nanocrystals in PGMEA by way of dynamic light scattering (DLS)

XRD and XPS analyses of the PTPG-2 and LTPF-1 nanoparticles show that the materials are crystalline anatase TiO_2 (Figure 2). The XRD pattern of the nanocrystals match those of a PDF reference, PDF 00-021-1272, for anatase TiO_2 (green lines). There were no changes in crystalline phase or peak shift to higher angle from anatase reference (due to lattice parameter decrease), which would be indicative of oxygen deficiency. No appearance of Ti^{3+} peak in the Ti 2p XPS spectra, which is closely associated with oxygen vacancies. Auger analysis does not show any differences between white stoichiometric control and Pixelligent samples.

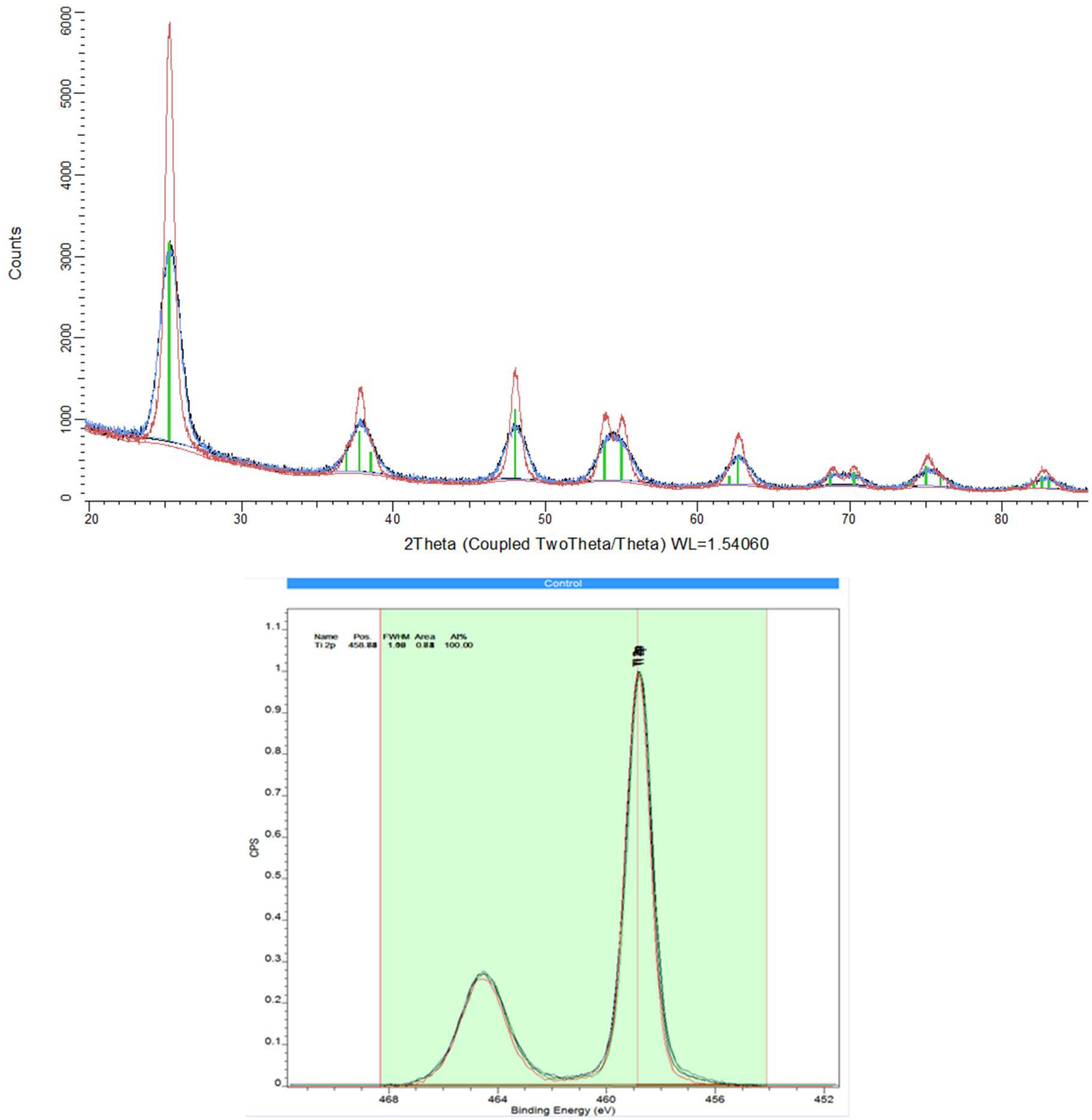

Figure 2. Top: Typical XRD patterns for PTPG-2 (blue) and LTPF-1 (red), reference PDF 00-021-1272, for anatase TiO_2 (green lines); Bottom: Ti 2p XPS data comparing a stoichiometric Control (red), PTPG-2 (blue) and LTPF-1 (black)

Methods

Dispersions

The nanocrystals, with their unique capping agents chemically bound to the nanocrystal surfaces, are dispersed in a PGMEA solvent at 50 wt%. Density measurements were taken of each dispersion by recording the weight of the dispersions in glass vials with an average volume of 1.942 cm^3. The measured dispersion densities of the PTPG-2 and LTPF-1 TiO_2 are 1.405 and 1.421 g/cm^3, respectively. From these values and additional information of the actual weight % solids in the PGMEA (0.97 g/cm^3) [5], the PTPG-2 and LTPF-1 capped nanocrystal densities were found to be 2.653 and 2.825 g/cm^3, respectively. These density values are necessary for converting weight loading to volume loading.

Formulations

Formulations were made by mixing the TiO_2 PGMEA dispersions with a UV-curable monomer Bisphenol A Glycerolate Dimethacrylate (BPA) at three different weight loadings. BPA has a reported liquid (uncured) refractive index of 1.557 at 589.3 nm [6]. A photoinitiator, Irgacure 819, was added at the concentration of 4 wt% with respect to the monomer. Viscosity was measured for each PGMEA formulation using a Brookfield RVDV-II+Pro viscometer with a CPA-40Z spindle. The viscosities and compositions of the formulations are reported in Table 1. Once films were deposited, dried of PGMEA and UV-cured, the PTPG-2 and LTPF-1 weight loadings were 50, 70 and 90%. The conditions used to make said films are described in the following paragraphs.

Table 1. Formulation viscosities and thicknesses for TiO2-BPA films

Film Name	TiO2 Wt%	BPA Wt%	PGA Wt%	Film Thickness (um)	Viscosity (cP)
50 wt% PTPG-2 in BPA	33.3	33.3	33.3	1.0 2.0 3.0	10.90
70 wt% PTPG-2 in BPA	41.1	17.8	41.1	1.0 2.0 3.0	8.35
90 wt% PTPG-2 in BPA	47.4	5.2	47.4	1.0 2.0 3.0	7.00
50 wt% LTPF-1 in BPA	33.3	33.3	33.3	1.0 2.0 3.0	9.38
70 wt% LTPF-1 in BPA	41.1	17.8	41.1	1.0 2.0 3.0	6.62
90 wt% LTPF-1 in BPA	47.4	5.2	47.4	1.0 2.0 3.0	4.74

Spin-coating conditions

Films were made on 2.5” x 2.5” precleaned glass substrates. Spin conditions were chosen to give 1, 2, and 3 um (± 0.2 um) films for each formulation at the different loadings. Table 1 summarizes the formulation viscosities. The spin conditions were altered for each sample to achieve desired film thicknesses.

Thermal Baking and UV conditions

After the films were deposited by spin-coating onto the glass substrates, they were prebaked for 1 min at 100°C on a hot plate. The films were then UV cured with a 385-nm UV LED lamp at a UV intensity of 0.13 W/cm^2 for 5 seconds at a total UV dose of 0.65 J/cm^2.

Measurements

The film transparency or %Transmission was measured with a UV-Vis spectrophotometer, and the film a*, b*, and Haze % were measured using a HunterLab Vista Hazemeter. A Metricon 2010/M prism coupler was used to determine the film refractive index (RI) at 3 points on each film at two wavelengths: 448 and 635 nm. The RI at 589 nm was calculated using the 448 and 635 nm values and the following equation for comparison across materials:

$$RI(589\,nm) = \frac{1}{6} * RI(448\,nm) + \frac{5}{6} * RI(635\,nm)$$

This expression was derived based on a two-term Cauchy equation [7] that represents the refractive index in relation to wavelength.

Results and Discussion

The transparencies of the TiO_2-BPA films for all three weight loadings at 2 microns are shown in Figure 3 represented as %Transmission across the visible light spectrum (with a glass substrate as the 100% baseline). For the PTPG-2 films %T values are above 90% for all three loadings above 400 nm. The LTPF film %T values are mostly greater than 90%, as well, apart from the 90% loading which falls slightly less than 90% around 400 nm. The 1- and 3-micron films (not shown) have similar data except for the 90% LTPF film. In the 3-micron thick films the 90% - LTPF %T falls to 87% at 400 nm. Pictures of the 2-micron films are displayed for visual reference against a white a black background for contrast in Figure 4.

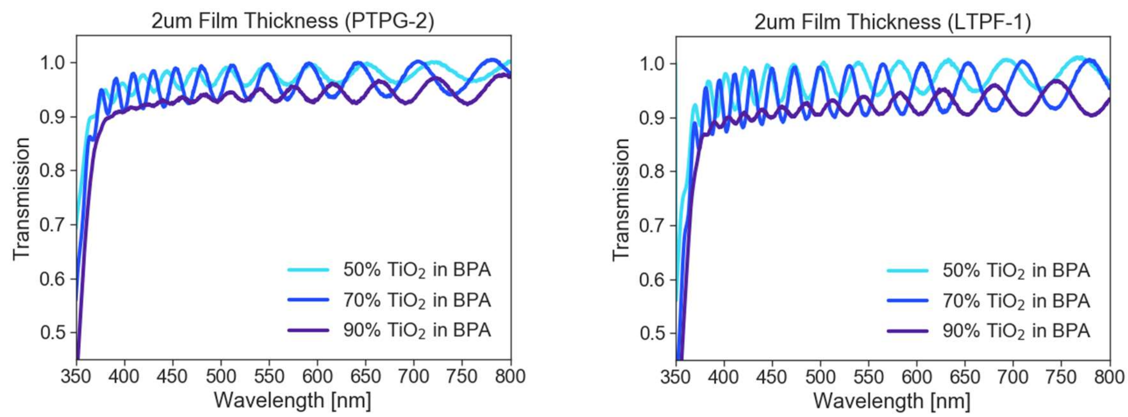

Figure 3. %Transmission in the visible light spectrum of 2-micron thick, spin-coated films with PTPG-2 and LTPF-1 in BPA monomer at 50, 70 and 90 wt% loadings

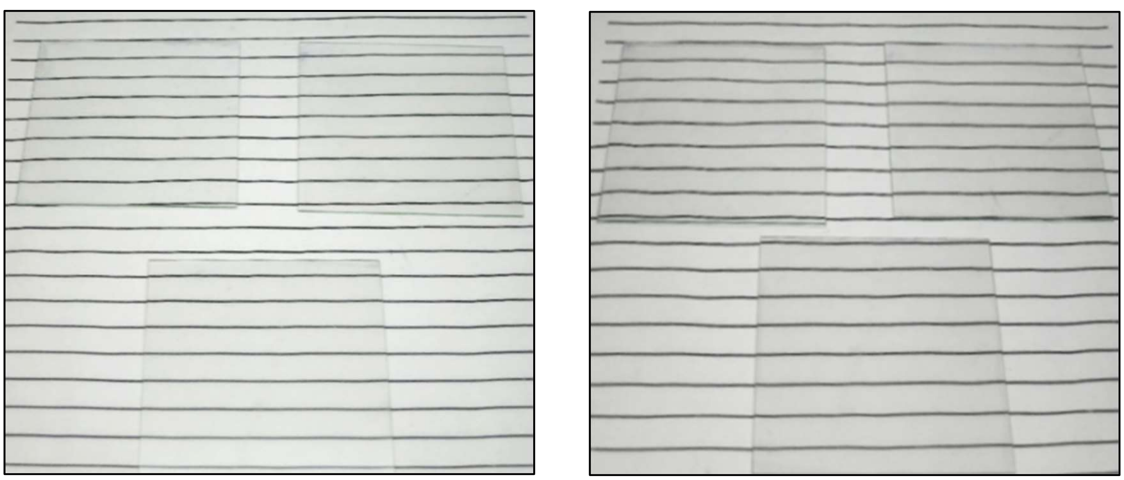

Figure 4. Pictures of 2-micron spin-coated films on glass for 50, 70 (top, left to right) and 90 (bottom) wt% loadings of PTPG-2 (left) and LTPF-1 (right)

In addition to the transparency and visual appearance of the TiO_2-BPA films, the %Haze (Transmission) was measured for each film. %Haze is directly related to a lack of transparency and scattering due to agglomerated particles within the films. A good indicator of a compatible dispersion of TiO_2 nanoparticles within a given monomer/binder system would be a low %Haze value. When compared against a glass reference, the films with both PTPG-2 and LTPF-1 at 50 and 70 wt% have %Haze values < 0.30% for film thicknesses between 1 and 3 microns. For the 90 wt% films slightly higher %Haze values were detected, specifically at 3 microns for the PTPG-2 film (0.60%) and 2- and 3-micron films for the LTPF-1 films (0.55 and 1.42%).

The color parameters a* and b*, which are components of the CIE L*a*b* color space, were measured for the TiO_2-BPA films to quantify any additional absorption. The a* and b* parameters depict the presence of green/red and blue/yellow colors, respectively. The a* and b* values are meant to be compared against a* = b* = 0. The TiO_2-BPA films at all TiO_2 loadings and film thicknesses with both PTPG-2 and LTPF predominantly show a* values that are < 0 or very slightly green (around -0.1 to -0.4). The b* values for all films are > 0 or slightly yellow (around +0.6 to +1.1). To compare against a reference, a 1.6-micron film with zirconia nanocrystals at 87 wt% in BPA was included in Table 2. %Haze and a* values for the ZrO_2 reference are very similar to the TiO_2-BPA films, and b* is slightly lower than the TiO2 films.

Table 2. %Haze, a* and b* values for TiO_2 and ZrO_2-BPA films

		PTPG-2			LTPF-1		
Loading Wt%	Film Thickness (um)	%Haze	a*	b*	%Haze	a*	b*
50	1.0	0.04	-0.29	0.70	0.09	0.05	0.72
	2.0	0.26	-0.24	0.73	0.10	-0.19	0.70
	3.0	0.06	-0.23	0.91	0.12	-0.21	0.88
70	1.0	0.08	-0.36	0.66	0.07	-0.21	0.88
	2.0	0.04	-0.27	1.01	0.17	-0.17	0.78
	3.0	0.07	-0.24	0.93	0.18	-0.21	0.98
90	1.0	0.37	0.50	0.69	0.33	-0.17	1.03
	2.0	0.20	-0.20	0.93	0.55	-0.12	0.98
	3.0	0.60	-0.20	0.95	1.42	-0.15	1.06
		10 nm ZrO_2 Reference					
87	1.6	0.20	-0.23	0.57			

Figure 5 shows how film refractive index increases with the incorporation of both PTPG-2 and LTPF-1 in BPA at different loadings. In the absence of the TiO_2 the BPA film RI is approximately 1.596 and 1.575 at 448 and 635 nm, respectively, when fully cured. The PTPG-2 increases the film RI to as much as 1.935 and 1.870 at 448 and 635 nm, respectively, when the nanocrystal loading is at 90%. In a similar manner, the LTPF-1 increases the film RI to 2.027 and 1.945 at 448 and 635 nm, respectively, at 90%. The overall changes in refractive index to the base BPA monomer are between 0.29 to 0.44 and depend on the nanocrystal used and wavelength.

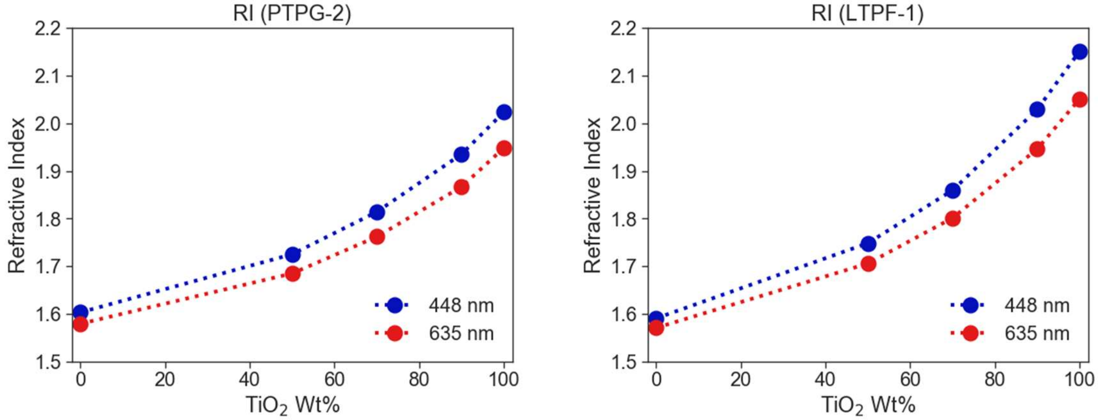

Figure 5. Refractive index values of TiO_2-BPA films versus TiO_2 weight percent at 448 and 635 nm wavelengths

Based on the density values determined for the TiO_2 nanocrystals, as described earlier, the weight loadings were converted into volume loadings so that RI could be plotted against volume percent. Figure 6 displays this data with linear fitted lines used to determine the RI of the TiO_2 alone. The PTPG-2 and LTPF-1 have RI values of 2.024/1.948 and 2.151/2.051 at 448 nm/635 nm, respectively. There is a clear particle size dependence on the film RI.

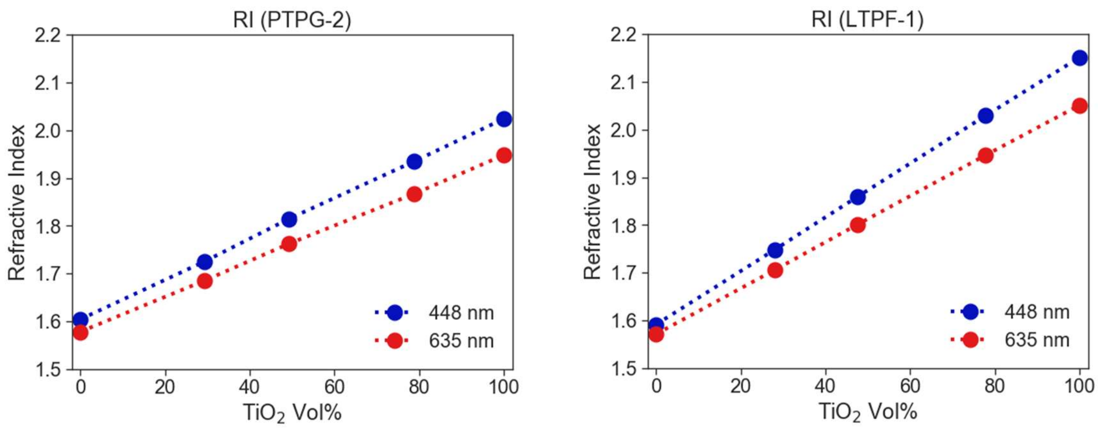

Figure 6. Refractive index values of TiO2-BPA films versus TiO_2 volume percent at 448 and 635 nm wavelengths

To compare the data better, the weight and volume loadings over the full range are tabulated with the corresponding RI values at 448, 589 and 635 nm in Table 3. This table is meant to be helpful for the reader when reviewing data and converting from TiO2 weight loading, which is a practical representation of concentration, to TiO_2 volume loading, which is useful for linear relationships with intrinsic properties (e.g. density and refractive index). The sodium D line wavelength (589.3 nm) is a common wavelength when comparing various refractive index values in industry. For the remainder of the paper, RI values are measured using only the 589 nm wavelength to simplify the comparisons.

Table 3. TiO_2-BPA Film Data Weight and Volume Loadings and RI

		PTPG-2			LTPF-1		
Wt%	Vol%	448 nm	589 nm	635 nm	448 nm	589 nm	635 nm
0	0	1.604	1.583	1.578	1.591	1.574	1.571
10	4	1.622	1.599	1.595	1.614	1.595	1.591
20	9	1.643	1.618	1.613	1.641	1.618	1.614
30	15	1.667	1.640	1.634	1.671	1.645	1.640
40	22	1.694	1.664	1.658	1.707	1.676	1.670
50	29	1.727	1.693	1.687	1.748	1.713	1.706
60	38	1.765	1.728	1.720	1.798	1.756	1.748
70	49	1.810	1.769	1.760	1.858	1.809	1.800
80	62	1.866	1.819	1.809	1.932	1.875	1.863
90	79	1.935	1.881	1.870	2.027	1.958	1.945
100	100	2.024	1.961	1.948	2.151	2.068	2.051

By using the RI values for the TiO_2 determined from the line-fitting and calculated at 589 nm, we can estimate potential film RI values with different monomers/resins. Figure 7 shows calculated values for RI with films made from monomers or resins with 1.600, 1.650 and 1.700 RI values at 589 nm. The graphs show that as the base monomer RI and TiO_2 loading increase, the change in film RI decreases. For example, at 50 vol % (approximately 70 wt%) with the PTPG-2, the RI difference between films using 1.60 RI and 1.70 RI monomers is about 0.050. For the same comparison at 75 vol% (approximately 88 wt%), the RI difference is only 0.025. With practical TiO_2 loadings (typically not greater than 90 wt%) with a 1.70 RI monomer, films with the PTPG-2 and LTPF-1 could achieve RI values as high as 1.91 and 1.99, respectively. One should note that these are calculated RI values. RI could be affected by the degree of crosslinking and different film thicknesses, and these aspects are not directly addressed in this paper.

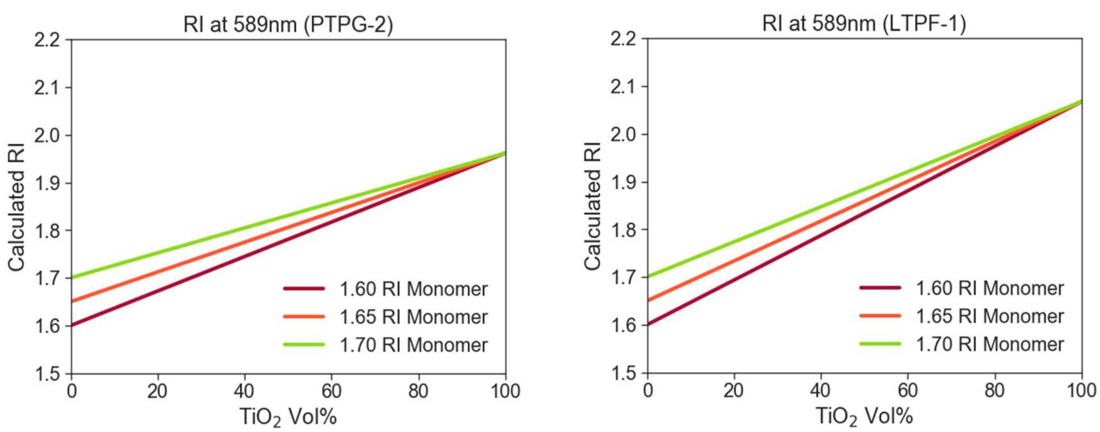

Figure 7. Calculated refractive index values of TiO_2-containing films with different RI values versus TiO_2 volume percent at 589 nm wavelength

Conclusions

Optical data for films comprised of Pixelligent's PixClear® TiO_2 nanocrystals, PTPG-2 and LTPF-1, dispersed within a 1.55 RI BPA dimethacrylate binder were reported and discussed. In general, films at 1 – 3-micron thickness show refractive index (RI) values between 1.69 – 1.96 at 589 nm, high transparency (>90%), low %Haze (< 1.0%), and (relative to similar ZrO_2 films) low color (a* ~ -0.2; b* < +1.0) for TiO_2 weight loadings ranging from 50 – 90%. Further information contained in this study shows the potential for higher RI values with monomer/binder systems with RI > 1.60. Maximum RI values at 90 wt% TiO2 loadings in a 1.70 RI monomer are estimated to be between 1.91 and 1.99 at 589 nm for both PTPG-2 and LTPF-1, respectively.

Please contact Richard Ming at Pixelligent Technologies rming@pixelligent.com for information on PixClear® TiO_2 dispersions.

References

[1] D. Hanaor and C. Sorrel, "Review of the anatase to rutile phase transformation," J Mater Sci, vol. 4, no. 46, pp. 855-874, 2011.

[2] Y. Cheng, C. Lu and B. Yang, "A Review on High Refractive Index Nanocomposites for Optical Applications," Recent Patents on Materials Science, vol. 4, no. 1, pp. 15-27, 2011.

[3] S. Katz, N. Kaplan, and I. Grossinger, "Using Diffractive Optical Elements," LTJ, vol. 15, pp. 29-32, 2018.

[4] 4. 1.-2. Recent Patents on Materials Science 2011.

[5] "Product data for product number 484431," Sigma Aldrich https://www.sigmaaldrich.com/catalog/product/sial/484431?lang=en&region=US

[6] "Product data for product number 494356," Sigma Aldrich, https://www.sigmaaldrich.com/catalog/product/aldrich/494356?lang=en&region=US

[7] "Cauchy equation," Wikipedia, https://en.wikipedia.org/wiki/Cauchy%27s_equation