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White Paper: Solvent-free Formulations with PixClear® ZrO_2 for High-Refractive Index Films

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Abstract

In this white paper, we demonstrate Pixelligent's PixClear® ZrO_2 nanocrystals (PCPG-2, PCPB-2, PCPC-1, and PCPR) in solvent-free formulations. Pixelligent's PixClear® ZrO_2 nanoparticles are compatible with a variety of acrylate, methacrylate, and vinyl monomers. Film refractive index values as high as 1.77 (589 nm) are possible with solvent-free formulations containing Pixelligent's PixClear® ZrO_2 nanoparticles and monomer systems with 1.60 – 1.70 RI. Formulation properties, such as viscosity and density, are reported in relation to ZrO_2 loadings to give perspective on process considerations for specific deposition techniques (e.g. inkjet printing). Density values in a benzyl acrylate monomer were shown to range from 1.1 to 2.5 g/cm3 at weight loadings of 0 to 80 wt%. Viscosity was shown to be highly dependent upon the choice of the ZrO_2 nanocrystal type and loading, as well as base monomer. Predicted viscosities are included in this paper to guide the reader in their formulating efforts with different monomers.

Keywords: zirconium dioxide, nanoparticle, nanocrystal, high refractive index, solvent-free

Introduction

PixClear® ZrO_2 Nanocrystals

Pixeligent's PixClear® ZrO_2 consists of four standard zirconium dioxide nanocrystals types, with 5-nm inorganic cores and an approximately 10-nm total particle diameters, in solvent-based dispersions at 50% by weight (wt%) ZrO_2. Figure 1 shows an example of the particle size, shape, and distribution. These four standard zirconia nanocrystals are compatible with various acrylates, and 1- and 2-part siloxane or low-molecular weight silicone, and epoxy systems. More exotic materials, such as episulfides and thiols, have also shown compatibility in recent applications. Acrylate systems are preferred based on Pixelligent's extensive materials research, knowledge, and experience with customers throughout the world.

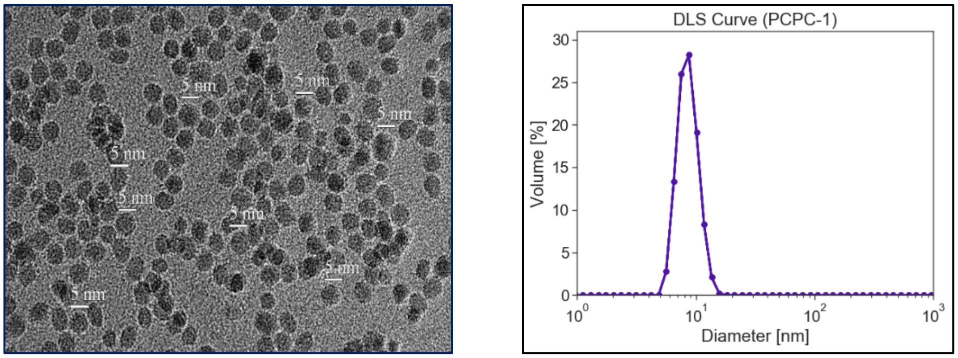

Figure 1. Core particle size of ZrO_2 nanocrystals by TEM (left) and particle size distribution curves for ZrO_2 nanocrystals by way of dynamic light scattering (DLS) (right)

PCPG-2

PCPG-2 is a ZrO_2 nanocrystal that possesses a non-reactive, highly dispersible capping agent with a demonstrated compatibility in many solvents and monomer systems. PCPG-2 is often the first nanocrystal chosen for customers to establish compatibility and clarity.

PCPB-2, PCPC-1, & PCPR

For customers interested in crosslinking in the final product customers are directed to these PCPB-2, PCPC-1, and PCPR. PCPB-2 offers a methacrylate-functional option that is applicable to many methacrylate- and acrylate-based formulations. The functionality of PCPB-2 can act as a crosslinker allowing customers to reduce or potentially eliminate conventional di-, tri-, and higher functional (meth)acrylate monomers in formulations. Refractive index, film hardness (and other mechanical properties), and degree of crosslinking can be tuned with adjustment of the loading of the PCPB-2.

PCPC-1 offers an acrylate-functional option that is also useful in methacrylate and acrylate-based formulations. Acrylates have higher reactivities than methacrylates, which could prove beneficial in combination with the appropriate monomers for applications requiring lower UV energy for cure.

PCPR has a similar capping chemistry as PCPB-2 but with a higher degree of surface coverage, which increases formulation stability, and final film chemical resistance. [1] All Pixelligent's Pixclear® ZrO_2 exhibit resistance to aggregation under normal conditions, however, PCPR offers additional protection by steric hindrance.

Pixelligent's PixClear® ZrO_2 dispersions are available in low-boiling point solvents, such as ethyl acetate (ETA). The ETA-based dispersions can easily be used in the creation of solvent-free formulations by solvent removal using a rotary evaporator (Rotovap). Solvent-free formulations remove the need for extra processing steps, such as baking, following film deposition. In this paper we will show that these formulations are highly sensitive to viscosity changes with the selection of specific monomers, oligomers, crosslinkers, and the ZrO_2 loading.

Pixelligent has successfully demonstrated the deposition of solvent-free nanocrystal formulations utilizing spin-coating, inkjet-printing, and slot die-coating. The viscosity of the solvent free formulation often determines the appropriate deposition method. The deposition of films from a solvent-free formulation is often more challenging than for solvent-containing formulations, however there are many compelling reasons to do so. Films demonstrate less shrinkage when deposited without solvent and for processes involving complex post-processing steps, like nanoimprinting, the solvent-free formulations are worth it.

Pixelligent offers a wide variety of other capped ZrO_2 nanocrystals that are also available upon request.

Methods

Formulations

Pixelligent's PixClear® ZrO_2 nanocrystals have demonstrated compatibility with acrylate, methacrylate, and vinyl monomers. Table 1 shows examples of different monomer that have shown compatibility with at least one type of the PixClear® ZrO_2 nanocrystals. These formulations were obtained by combining the nanocrystals already dispersed in a low boiling point solvent with the chosen monomers and then removing the solvent.

Many photoinitiators and photosensitizers have been found to be compatible with Pixelligent's ZrO_2 formulations. Examples include Irgacure 184, Irgacure 819 (BAPO), Ebecryl P39, Ebercryl P115, 2-Isopropylthioxanthone (ITX), TPO and TPO-L. The films can be cured with a broadband UV source (Dymax 5000-EC Mercury Vapor) or with a 385-nm UV LED system (Dymax BlueWave® LED Flood) depending on the photoinitiator selected. Typical UV exposures range from 1 – 10 J/cm^2 under an air atmosphere. Although not covered in this white paper, formulations cured effectively under inert (e.g. nitrogen) conditions.

In this paper, Irgacure 819 has been utilized as the photoinitiator at a concentration of 4 wt% with respect to the monomer.

Table 1. List of monomers compatible with PixClear® ZrO_2

Chemical Name	Abbreviation	Viscosity @ 25°C (cP)	RI @ 589 nm	Reactive Functionality
Benzyl (Meth)Acrylate	BA	2.6	1.514	Acrylate
Ethylene Glycol Phenyl Ether (Meth)Acrylate	PEA	9.6	1.518	Acrylate
Diethylene Glycol Dimethacrylate	DEGDMA	12.0	1.463	Acrylate
Trimethylolpropane Tri(meth)acrylate	TMPTA	130	1.474	Acrylate
Phenoxy Benzyl Acrylate	PBA	16.2	1.565	Acrylate
o-Phenylphenol Ethylene Oxide Acrylate	OPPEOA	130	1.577	Acrylate
Biphenyl Methyl Acrylate	BPMA	30	1.600	Acrylate
Styrene	STY	0.8	1.547	Vinyl
N-Vinyl Pyrrolidone	NVP	2.5	1.512	Vinyl
N-Vinyl Caprolactam	NVC	Solid	1.548	Vinyl
Vinyl Cinnamate	VC	5.0	1.567	Vinyl
Divinyl Benzene	DVB	1.0	1.561	Vinyl
9-Vinyl Carbazole	NVCB	Solid	1.683	Vinyl

Measurements

Formulation viscosity was measured using a Brookfield RVDV-II+Pro viscometer with a CPA-40Z spindle. Surface tension and contact angle values of the monomer and formulations were determined with a Ramé-Hart Model 210 Goniometer / Tensiometer using the pendant and sessile drop methods.

For cured films, the light transmission (%T) from 350 to 800 nm was measured with a UV-Vis spectrophotometer. A Metricon 2010/M prism coupler was used to measure the refractive index (RI) and film thickness using two wavelengths (448 and 635 nm) at 3 different spots on each film and the results are presented in Figure 2. The RI at 589 nm was calculated from the measured RIs at 448 and 635 nm and the following equation derived from the two-term Cauchy equation [2].

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

To illustrate achievable RI values for formulations comprising Pixelligent's ZrO_2 nanocrystals, Figure 2 shows estimated values in resins with 1.600, 1.650 and 1.700 RI values [1]. Conventional monomers can easily achieve a base RI close to 1.600 at 589 nm when cured. Newer, more exotic monomers exist or are currently under development with multiple suppliers with even higher RI values. For example, NTT-ATT manufactures two resins that have 1.68 RI (589 nm) at 9 cP and 1.72 RI (589 nm) at 20 cP respectively [3]. Due to limitations in viscosity and inkjet printing, typical ZrO_2 weight loadings are between 35 – 55 wt% or approximately 15 – 30 vol%. The viscosity of the monomers is very important and determines which ZrO_2 loading is appropriate for an application. Figure 2 shows that film RI values of 1.63 – 1.75 are obtainable with volume loadings in the range of 15 – 30 vol% for monomers with RI values between 1.600 and 1.700.

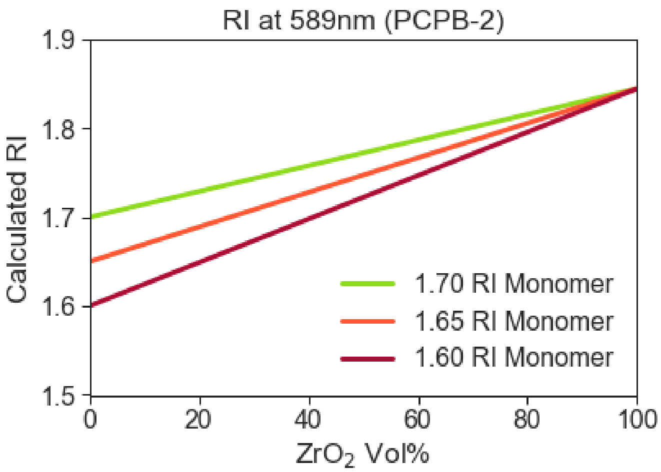

Figure 2. Calculated refractive index values of PCPB-2-containing films with different RI values versus percent at 589 nm wavelength

Results and Discussion

Formulation Data

When developing solvent-free formulations with nanocrystals, it is often important to know the liquid density. Inkjet printing, for example, is highly dependent on material properties of the formulation, such as viscosity, surface tension and density. These properties affect the ejection of the liquid droplets, as well as, the shape and formation of ligaments and satellites. Figure 3 shows the liquid density of PCPC-1 ZrO_2 nanocrystals in a benzyl acrylate (BA) monomer at many loadings. Density values range from about 1.1 to 2.5 g/cm^3 over the PCPC-1 loading range of 0 to 80 wt%. To demonstrate the linear relationship between density and ZrO_2 volume loading, a second graph in Figure 3 has been included. Volume percent will come up again in this paper with regards to formulation viscosity and film refractive index.

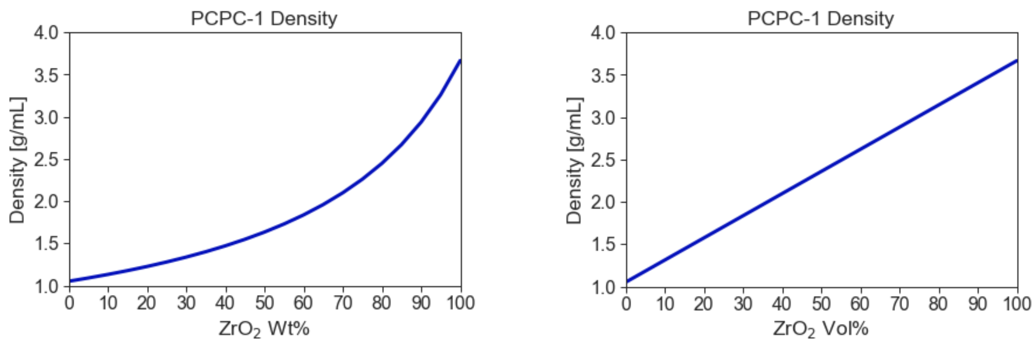

Figure 3. Density of PCPC-1 ZrO_2 in BA versus Wt% (left) and Vol% (right)

Formulation viscosity increases with nanocrystal loading. Figure 4 shows the viscosity behavior of PCPC-1 in BA. The left graph represents measured data of the viscosity changes at different weight loadings between 50 and 75%. For a low-viscosity monomer, such as BA, viscosity values can be less than 200 cP for formulations with as much as 72 wt% ZrO_2 loading (roughly 42 vol%). In the right graph, measured viscosity data points were fitted with a curve using linear least-squares regression as a function of PCPC-1 vol%.

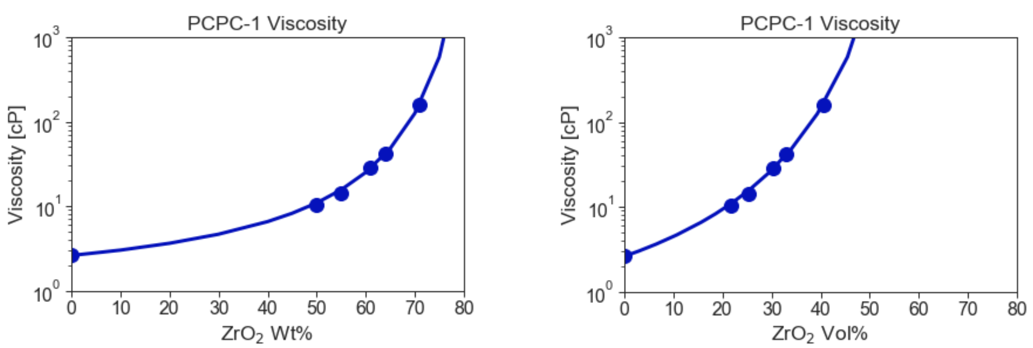

Figure 4. Viscosity of PCPC-1 ZrO_2 in BA versus Wt% (left) and Vol% (right)

The fitted equation, derived by Mooney [4] for high concentrations of particles has the following form:

$$\mu = \mu_0 exp\left[\frac{k\varphi}{1-\frac{\varphi}{\varphi_m}}\right]$$

The parameters of the Mooney equation are μ (formulation viscosity), μ_o (base monomer viscosity), k (a fitted constant), φ (PCPC-1 volume percent) and φ_m (the maximum packing fraction which is also a fitted constant). k and φ_m values of 4.7 and 74.8% agree with the experimental data. The use of the Mooney equation allows for the viscosity of a wide range of formulations to be predicted. The viscosity of formulations with Pixelligent PixClear® ZrO_2-loaded at 70 – 80% shows dramatic changes with even 1 – 5 wt% increments in loading. At volume fractions of 75% ZrO_2, formulations start to exhibit semi-solid characteristics in agreement with the fitted maximum packing fraction from the Mooney equation. Deposition of films with loadings as high as 90 wt% or 75 vol% have proven possible, but they require solvent addition for film deposition. [1]

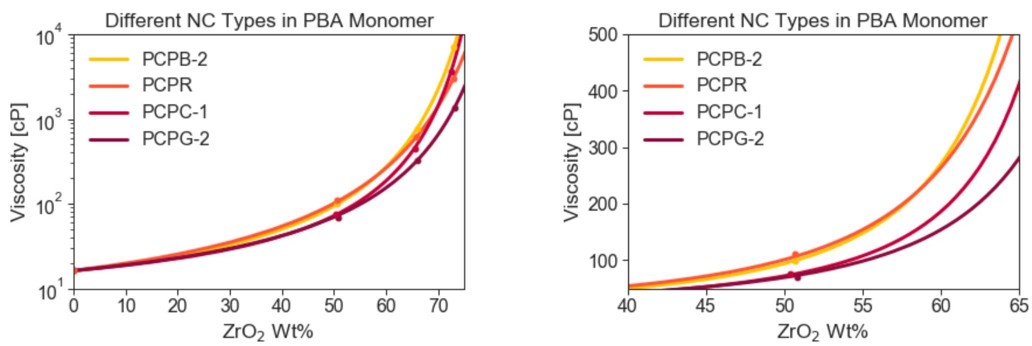

Figure 5. Viscosity ratio versus Wt% of PCPG-2, PCPB-2, PCPC-1 and PCPR ZrO_2: Full range (left) and narrow range (right)

Figure 5 compares the viscosity of PCPG-2, PCPC-1, PCPB-2, and PCPR in a PBA monomer (See Table 1) at different loadings. The figure demonstrates that viscosity is different depending on the capping chemistries. For all the formulations a gradual increase in viscosity from the base monomer value of 16 cP at 0 wt% to approximately 100 cP at 50 wt% is shown. In the narrow-range graph, the viscosities can be seen to vary between 69.3 to 100.7 cP. The PCPG-2 ZrO_2 has the lowest viscosity, while the PCPR ZrO_2 has the highest. As the ZrO_2 loading increases the PCPG-2 maintains the lowest viscosity. The PCPR ZrO_2 shows lower viscosity values than the PCPB-2 and PCPC-1 at loadings greater than 60 wt%.

As a guide for making formulations using Pixelligent PixClear ZrO_2, the viscosity of formulations with various monomers and PCPC-1 are plotted in Figure 6. The y-axis is represented as the viscosity ratio, which is the ratio of the formulation viscosity divided by the base monomer viscosity. As can be seen from the figure, the data collapses onto a single curve. The Mooney equation with a φ_m value of 87% was used to apply a fitted curve as a guide. Thus, by knowing the monomer viscosity, one could estimate formulation viscosities at specific weight loadings. For example, a PCPC-1 loading of 60 wt% yields a predicted viscosity ratio close to 12. These 60 wt% formulations made with monomer viscosities of 5, 20, and 50 cP would then have viscosities 60, 240, and 720 cP, respectively. Most of the data in Figure 6 resides between 35 and 60 wt%, and predictions tend to be within 10 – 20% of the experimental values. At higher PCPC-1 loadings the model breaks down because of the stronger dependence of viscosity on The data and fitted curve in Figure 6 are specific to the PCPC-1 ZrO_2 nanocrystals and different zirconia products can affect the formulation viscosity as shown in Figure 5. Significant viscosity differences start to occur in formulations made with different nanocrystals can start to be seen for loadings above 50 wt%.

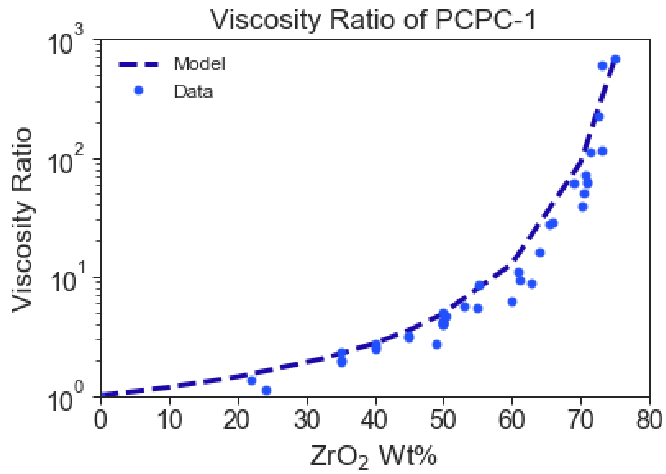

Figure 6. Viscosity ratio versus Wt% of PCPC-1 ZrO_2

Knowledge of the viscosity at 25 °C is often enough for most applications, however, certain applications allow for heating steps to mitigate high formulation viscosities. As an additional guide, Figure 7 displays the temperature dependence of four formulations with PCPC-1. Inks 1 to 4 are nanocomposite formulations with PCPC-1 weight loadings between 40 and 70 wt%. The 25 °C viscosity values of Ink 1 to 4 are approximately 180, 55, 30, and 10 cP respectively. These inks represent different examples of the required printhead temperatures needed to achieve inkjettable viscosities, approximately 5 – 20 cP depending on the type of printhead. From a practical point of view, Ink 1 may not be easily inkjettable

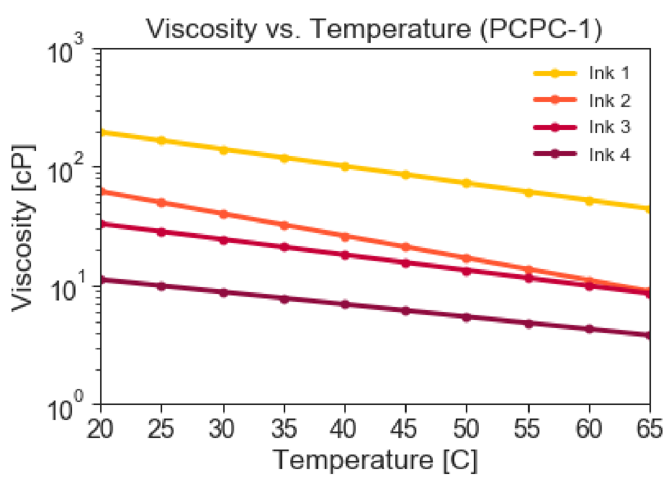

Figure 7. Viscosity of Inks comprising PCPC-1 with different monomers at different loadings

since temperatures greater than 65 °C are needed. In addition to possessing appropriate viscosities, printhead temperature must be minimized for a given formulation to prevent loss of any volatile components in the formulation that could, over long periods of time, lead to nozzle clogging. Inks 2 to 4 represent more characteristic examples that can be heated to modest temperatures such as 30 – 50 °C and maintain inkjettable properties.

Surface tension is often an important property of the formulation, especially when considering inkjet-printing depositions and substrate wetting. Most of the monomers tested and formulated with had surface tensions between 35 and 40 dyne/cm (See Table 2). When prepared with the PCPC-1 nanocrystals at weight loadings of 40 and 50%, the surface tension values in M1 and M2 monomers did not change significantly. Similarly, the contact angle values measured on glass (hydrophilic) and Teflon (hydrophobic) for the nanocomposite formulations did not vary from the monomers alone. Upon addition of a surfactant, BYK 378, noticeable changes in surface tension and contact angle were observed. At 21 – 22 dyne/cm, the nanocomposite inks were inkjettable and very wettable to glass substrates. Other surfactants, such as BYK 333 and FLOWLEN G-700, have been tested with other nanocomposite formulations not shared in this paper and have surface tension values between 25 and 30 dyne/cm. Depending on the printhead being used, the target surface tension of the formulation will vary. The DMP 2800 User's Guide (Version 2) recommends a value between 28 and 33 dyne/cm.

Table 2. Surface tension of formulations containing PCPC-1 ZrO_2, BA, PBA, PEA and/or NVP and BYK 378

Formulation	Surfactant	Surface Tension (dyne/cm)	Contact Angle (degrees)	
			Glass	Teflon
BA	None	36.7		68.7
PEA	None	38.4	17.4	72.2
PBA	None	42.0	23.5	82.8
NVP	None	38.1		71.9
40%PCPC-1 in M1	None	36.1	22.4	72.7
40%PCPC-1 in M1	1% BYK 378	21.0	25.8	36.0
50%PCPC-1 in M2	None	35.4		71.9
50%PCPC-1 in M2	1% BYK 378	22.0		36.0

Film Data

For spin-coating applications of solvent-free nanocomposite formulations, Figure 8 demonstrates the spin speed conditions used to achieve specific film thicknesses for solvent-free formulations over a range of viscosities. Fitted equations are provided for 500, 1000 and 2000 RPM spin speeds to estimate film thicknesses for a given viscosity.

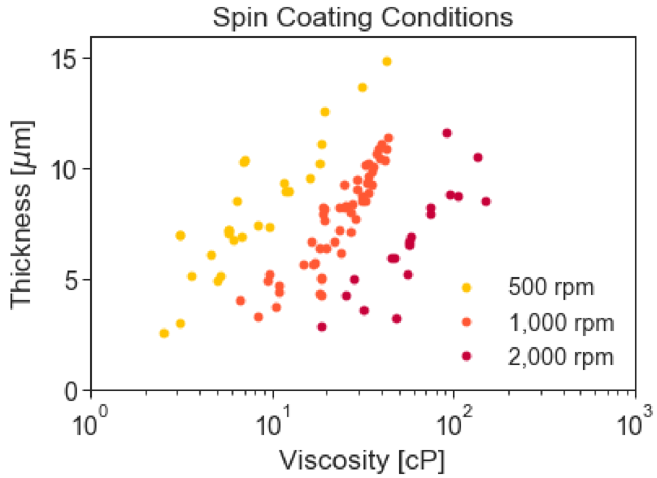

Figure 8. Semilog plot of film thickness versus spin speed for different viscosities

Nanocomposites comprised of the Pixelligent PixClear® ZrO_2 nanocrystals yield clear high-refractive index films with excellent transparency. Using a Dimatix DMP 2800 desktop inkjet printer with 10-pL cartridges, a formulation comprising PCPC-1 ZrO_2 and a blend of acrylic monomers and surfactants was printed onto a glass substrate. Figure 9a shows the high transparency of the 10-micron film from 400 – 800 nm. This ink produced a film with visual clarity and good edges and corners on a glass substrate, as shown in Figure 9b.

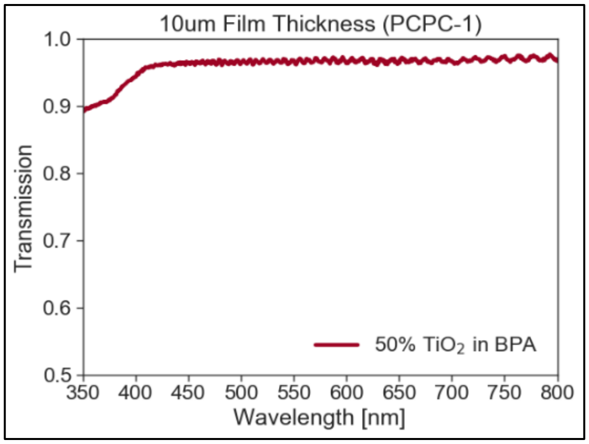

Figure 9. a. %T in the visible light spectrum of a 10-micron thick and b. an inkjet-printed film photographed on a Silicon wafer

Conclusions

Solvent-free formulations comprised of Pixelligent's PixClear® ZrO_2 nanocrystals, PCPG-2, PCPB-2, PCPC-1, and PCPR are reported and discussed. Useful guidelines, examples, and properties have been shared to help guide the selection of ZrO_2 nanocrystals, compatible monomers, photoinitiators, and surfactant choices.

Please contact Richard Ming at Pixelligent Technologies (rming@pixelligent.com) for information on solvent-free formulations with PixClear® ZrO_2 for high-refractive index films.

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