White Paper: Compatibility of ZrO2 Nanocrystals in Acrylic Monomers

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Abstract

This white paper illustrates the optical clarity and compatibility of four PixClear® nanocrystal dispersions (PCPG-2, PCPB-2, PCPN and PCPR) in nine different acrylate monomers with varying chemistries and molecular weights. Propylene glycol monomethyl ether acetate (PGMEA) was the solvent used for this study. The incorporation of PixClear® high refractive index zirconia nanocrystals (< 10 nm in diameter) into various polymeric materials enhances optical performance without affecting the processibility or physical qualities that are desired. PixClear® zirconia nanocrystals have organic molecules at the surface known as capping agents. The interaction between these capping agents and the dispersion matrix (either solvent or polymer) determines the quality of the dispersion. Good visual clarity and low OD values resulted were obtained for acrylates with MW values ranging from ~200 to 1,000 g/mol and chemical backbones consisting of a variety of chemical groups: aliphatic, cycloaliphatic, polyester, bisphenol A, propylene glycol and aliphatic urethanes.

Introduction

The combination of high refractive index, optical clarity/transparency, and low haze is very challenging to achieve in polymers and nanocomposites. Good optical clarity is often the most important property of films and other structures intended for high value optoelectronic applications in display, lighting and optics. High clarity is defined as little or no scattering (i.e. light does not deflect back or in undesirable directions), and low light absorption. Nanocomposites consisting of polymers and PixClear® zirconia nanocrystals can offer the processing properties of polymer systems along with a combination of high refractive index and clarity that are unattainable in pure polymer systems, but many considerations are required for optimization. Scattering in a nanocomposite is often caused by the index mismatch between the two materials, and is exacerbated by large particles or aggregates of smaller particles within the matrix{1}. For nanocomposite systems, the particle size is preferred to be less than 40 nm (e.g. 1/10 the wavelength of blue light) such that any scattering that occurs is within the Rayleigh scattering regime {2}. Large particles scatter all wavelengths of light uniformly under the Mie scattering regime. Mie scattering is observed for agglomerated nanoparticle systems in which the scale of the aggregates and agglomerations are hundreds of nanometers.

By engineering the surfaces of zirconia nanocrystals using capping agents, PixClear® nanoparticles maintain good dispersibility while significantly reducing the tendency to cluster/aggregate within polymeric systems. Pixelligent's PixClear® nanodispersions contain zirconia nanocrystals that are < 10 nm in size with a very narrow size distribution. The surfaces of these nanocrystals are well-passivated by capping agents which prevent aggregation and offer compatibility in many different solvents, monomers and polymers even at very high nanoparticle loadings up to 90wt%.

For this study, nine acrylic monomers were selected to better elucidate the relationship between the monomer and nanocomposite clarity (Table 1). The acrylates were chosen because of their different chemical functionality and molecular weight/viscosity.

Acrylate Monomer	Monomer Provider	Chemical Backbone	Estimated MW (g/mol)	Viscosity (cP)	
				25°C	>25°C
SR238B	Sartomer	Hexanediol	200	9	
SR306F	Sartomer	Propylene Glycol	300	15	
SR833S	Sartomer	Cycloalkane	300	130	22 (60 C)
CR-424	PPG Industries, Inc.	Propylene Glycol		160	
BPA	Sartomer	Bisphenol A	500		1,380 (70 C)
CN2283	Sartomer	Polyester-Aromatic	> 600		25 (60 C)
CN2281	Sartomer	Polyester- Bisphenol A	700	1,000	
CN2003B	Sartomer	Polyester- Bisphenol A	1,100	145,000	3,250 (60 C)
CN2920	Sartomer	Aliphatic Urethane			25,000 (60 C)

Table 1. Diacrylate monomers {3} with different chemical backbones and molecular weights (MW).

Methods

Four Pixelligent PixClear® capped nanocrystals (PCPG-2, PCPB-2, PCPN and PCPR) were dispersed into various test acrylate monomer solutions (see Table 1) with PGMEA solvent. PixClear® PCPG-2 and PCPN dispersions consist of capping agents with tails that are non-functional. The PCPB-2 and PCPR dispersions contain capping agents with functional moieties able to undergo acrylic crosslinking (PCPB-2 and PCPR). Additional information on PixClear® materials is available at www.pixelligent.com.

Solutions of acrylate monomers and PixClear® nanocrystal dispersions were separately prepared at 40 and 50 wt% in PGMEA, respectively. The mixtures were prepared to give 1:1 ratio of ZrO2 to monomer. Each acrylate monomer consists of a chemical backbone (as stated in Table 1) and two acrylate functional end groups. 8 of the 9 acrylate monomers were acquired through Sartomer {3}. The CR-424 acrylate was provided by PPG Industries, Inc.

Sample preparation

3-g samples were prepared by adding 1.33 g of nanocrystal dispersion with 1.67 g of acrylate monomer solution. Samples were mixed via vortexing in a small glass vial for 1 minute. The wt% of zirconia nanocrystals in the total dispersion was 22.2%. The remaining 77.8 wt% is 22.2 wt% acrylate and 55.6 wt% PGMEA. Figure 1 shows examples of the varying degree of clarity and haziness observed for some of the dispersions.

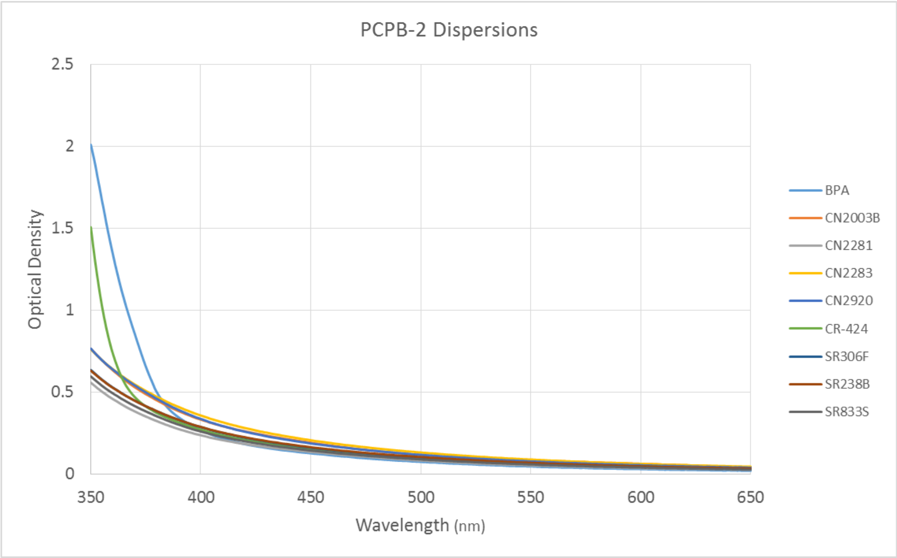
Figure 1. Top picture, PGMEA solvent in a cuvette. Below, examples of PixClear® dispersions with different compatibility levels: clear, slightly hazy to very hazy. All cuvettes have 1 cm path length.

Instrumentation

Aliquots of the dispersions (zirconia nanocrystals, acrylate monomer and PGMEA solvent) were transferred into a cuvette, and the optical density was measured in a Perkin Elmer Lambda 850 UV/Vis spectrophotometer. The optical density (OD) values were measured from 350 to 650 nm. The dispersions were also evaluated by eye to add a visual clarity observation to the OD values.

Results and Discussion

The measured OD versus wavelength curves for both PCPB-2 and PCPN dispersions are displayed in Figure 2. Some differences in the curves are due to the acrylate itself, while other differences are characteristic of the interaction between the capped zirconia nanocrystals and the monomer. For example, both the BPA and CR-424 monomers for the PCPB-2 and PCPN systems have abrupt increases in OD below 400 nm because of the absorption of the monomers in the UV wavelength range. By comparison, the other acrylates typically exhibit much lower OD values from 350 to 650 nm. The PCPB-2 dispersions demonstrate excellent clarity and low OD (< 0.5) between wavelengths of 400 and 650 nm. The capping agents on the surface of the nanocrystals are effective at creating sufficient steric (and possibly electrostatic) stabilization to prevent the formation of aggregates/agglomerates. Additionally the interaction between the matrix and the capping agents must be favorable enough to drive the system towards maximizing this interface {4}.



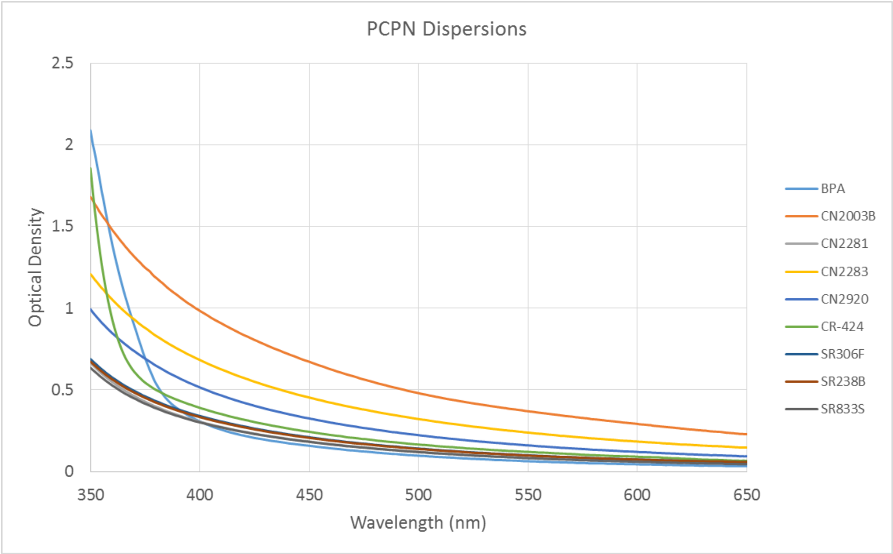


Figure 2. OD versus wavelength curves for 22.2 wt% loading PCPB-2 and PCPN with 22.2 wt% acrylate and 55.6 wt% PGMEA (1:1 NC: acrylate ratio)

For the PCPN dispersions six of the OD curves agree well with the PCPB-2 curves, evincing comparable OD values at the same wavelengths. However, the CN2920, CN2283 and CN2003B acrylates with PCPN have slightly higher OD values over the same dispersions for PCPB-2. Even though the dispersions demonstrated good visual clarity, some shift in OD is observed with the UV-Vis measurement. This type of shift is indicative of some scattering at each wavelength. Subtle indications such as these can help one to evaluate various monomers for a given application to choose the best compatibility/dispersibility in addition to other important properties (e.g. refractive index of nanocomposite, flexibility, rheology {5}, mechanical strength {6}, etc.).

	BPA			SR306F			SR833S		
PixClear® NC	350 nm	400 nm	650 nm	350 nm	400 nm	650 nm	350 nm	400 nm	650 nm
PCPG-2	2.002	0.267	0.032	0.555	0.254	0.027	0.658	0.342	0.115
PCPB-2	2.009	0.270	0.022	0.636	0.288	0.033	0.597	0.261	0.029
PCPN	2.089	0.307	0.033	0.689	0.340	0.057	0.635	0.301	0.046
PCPR	1.916	0.196	0.009	0.699	0.309	0.030	0.642	0.270	0.024
	SR238B			CR-424			CN2281		
PixClear® NC	350 nm	400 nm	650 nm	350 nm	400 nm	650 nm	350 nm	400 nm	650 nm
PCPG-2	0.552	0.252	0.025	1.430	0.237	0.023	0.505	0.211	0.019
PCPB-2	0.632	0.289	0.035	1.506	0.272	0.032	0.559	0.239	0.028
PCPN	0.673	0.333	0.059	1.857	0.390	0.066	0.665	0.305	0.047
PCPR	0.691	0.305	0.029	1.600	0.280	0.022	0.692	0.291	0.036
	CN2283			CN2003B			CN2920		
PixClear® NC	350 nm	400 nm	650 nm	350 nm	400 nm	650 nm	350 nm	400 nm	650 nm
PCPG-2	0.605	0.276	0.029	0.709	0.301	0.034	0.461	0.191	0.271
PCPB-2	0.763	0.359	0.047	0.765	0.334	0.043	0.766	0.338	0.041
PCPN	1.209	0.683	0.147	1.681	0.984	0.229	0.994	0.515	0.094
PCPR	1.069	0.525	0.073	4.157	4.686	3.740	1.573	0.796	0.135

Table 2. OD values at 350, 400, and 650 nm for total dispersions with test acrylates in PGMEA: green denotes clear dispersions and red indicates incompatibility

Table 2 is a summary of all of the OD data specifically at 350, 400 and 650 nm wavelengths for all four dispersions with the nine acrylate solutions in PGMEA. These data are also color coded to denote visual clarity (nearly all cases) and one example of incompatibility. As seen in Figure 2 some nanocrystal-acrylate pairings led to higher OD values as compared with other nanocrystals with the same acrylate. For example, acrylates CN2283, CN2003B and CN2920 gave lower OD values with PCPG-2 and PCPB-2 than with PCPN and PCPR. These monomers, according to Table 1, happen to have the highest MW and viscosities of the group and may induce minor agglomeration of the nanocrystals. Again, these dispersions are visually clear but they have noticeably higher OD values. Although the clarities are quite good for nearly all samples (similar to middle left picture in Figure 1), PCPG-2 stands out among the group of PixClear® zirconia nanodispersions as the most compatible, showing the lowest OD values in the majority of tests with acrylate monomers. These results show that the type of capping agent can have an important impact on compatibility with a given monomer.

Conclusions

The Pixelligent PixClear® zirconia nanocrystals PCPG-2, PCPB-2, PCPN and PCPR in PGMEA solvent display wide compatibility with acrylates of different MW and chemical functionality. Good visual clarity and low OD values resulted for acrylates with MW values ranging from ~200 to 1,000 g/mol and chemical backbones consisting of a variety of chemical groups: aliphatic, cycloaliphatic, polyester, bisphenol A, propylene glycol and aliphatic urethanes. Our results demonstrate that Pixelligent's capping technology is capable of producing non-aggregating nanocrystals, but that matching correct capping agent chemistry with a particular acrylate is required for the best material outcomes. These conclusions are encouraging and demonstrate the versatility of Pixelligent's zirconia nanotechnology. Future studies will address new monomer and polymer chemistries and their respective compatibility with current nanocrystals and nanocrystals with different capping agents on the surface.

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