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IMPRINT

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ABSTRACT

In a variety of applications, non-yellowing, easy-processable bulk materials with high refractive indices (> 1.6) are needed in order to improve performance and/or efficiency of optical and electro-optical devices and components. Facing these demands, most common approach is the use of composite material consisting of a polymeric matrix and high-refractive nanoparticles. This white paper discusses the combination of best-of-class materials in order to achieve high-quality composites showing a remarkable ageing stability. The blue-light stability and the achievable refractive indices are reported.

INTRODUCTION

This white paper will summarize recent results of the combination of ORMOCER® matrix materials and PixClear® ZrO_2 nanocrystals for the formulation and preparation of new high index films. These films typically find application in (O)LED displays and lighting, as ITO index matching coatings. Especially for the light outcoupling from InGaN-based LED chips the availability of chemically and thermally stable highly transparent high refractive index casting materials is of strong interest. The materials used for that purpose so far – mainly epoxy or silicone resins – are lacking of photochemical stability and are limited in the possible refractive index. The approach to use high-index ORMOCER® matrix materials for the synthesis of composites together with stable and monodispersed ZrO_2 nanocrystals yields several advantages over conventional composites using silicone materials, as will be discussed in the following sections. Typical drawbacks of previously used material solutions contained critical film thickness and coating capabilities, insufficient storage stability and restricted UV stability of the matrix materials.

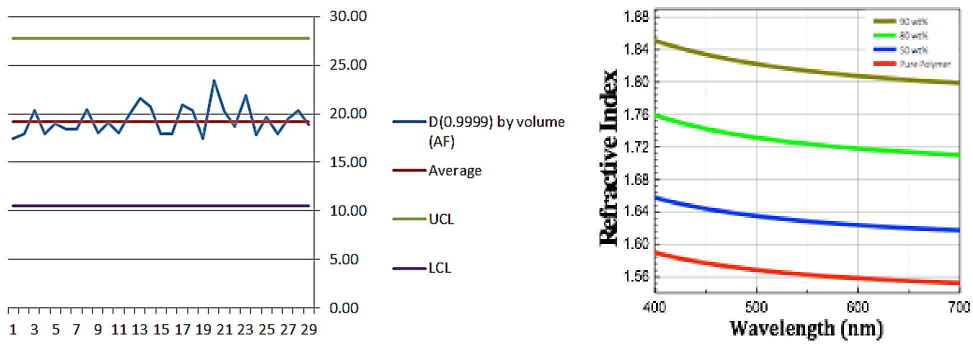


Figure 1

Left: Typical statistical process control chart of D9999, the largest diameter in nm of 99.99% of particles by volume.

Right: Refractive index of cured zirconia nanocomposites and as a function of wavelength and loading in BIS-GMA formulations.

MATERIAL BACKGROUND

PixClear®

Pixelligent's PixClear® products are high performance ZrO_2 nanocrystal dispersions that are high refractive index and highly transparent. ZrO_2 nanocrystals are less than 10 nm in size and their surfaces are well passivated with Pixelligent's proprietary capping agents to give best compatibility with various solvents, monomers and polymers. These nanocrystals are monodisperse with no aggregations and typical D9999 numbers of < 30 nm (Figure 1, Right). Due to the high quality of the dispersions, the nanocrystals have minimal effect on the viscosity and transparency of the formulations even at very high nanocrystal loading, such as >70wt% reaching (RI as high as 1.85 (Figure 1, Left). This is especially important for high refractive index solvent free formulations where aggregation or large particle size causes extreme viscosity increase and limits the processability of the materials.

ZrO_2 is one of the highest refractive index and transparent materials. It has a bulk refractive index of 2.2 and a wide bandgap which makes it transparent in the visible wavelength range. Compared to its higher refractive index counterpart, TiO_2, ZrO_2 is not photoactive and hence more stable than TiO_2. Due to the combination of these properties - high refractive index, transparency, monodispersity, and chemical stability- ZrO_2 nanocrystals are the best materials to increase the RI of high performance polymers, especially in displays and lighting markets.

Pixelligent has developed a wide variety of capping agents to ensure compatibility between the zirconia nanoparticles and materials commonly used to create optical resins and films such as acrylics, epoxies, urethanes and silicones. Compatibility between nanocrystal capping and the binder matrix enables a high nanoparticle loading while minimizing any increases in viscosity. These capping agents can also be designed for interaction with the matrix material through crosslinking groups. Throughout the development and scale-up of PixClear® capped nanocrystals to the multi-ton level, tight control of capping chemistry has been established to accompany the process controls around nanocrystal size and optical clarity.

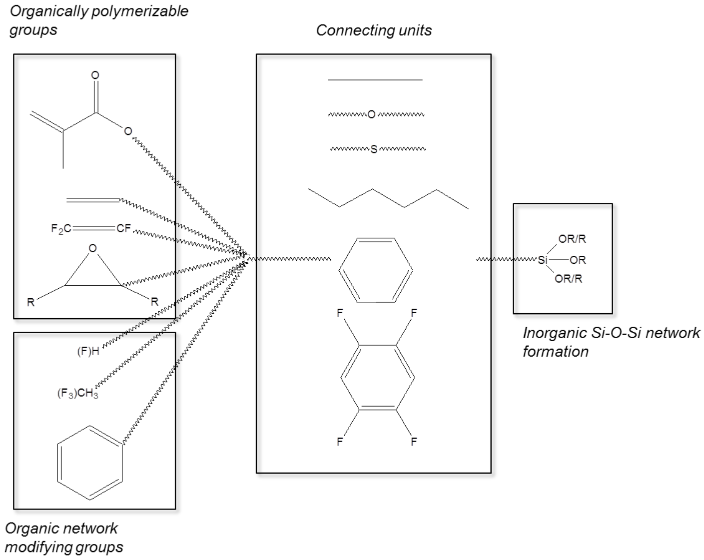
PixClear® nanocrystals enable refractive index tuning of optical materials without the typical trade-offs associated with composite formulations, such as increased haze, large viscosity gains and lower clarity. By aiming to achieve excellent compatibility in a wide range of commonly used optical materials through intelligent capping design, PixClear® ZrO_2 has brought many benefits to end-users seeking improved light extraction through performance additives. Pixelligent's materials have been scaled up to multi-ton volumes, supporting applications in OLED display, OLED lighting, HD display, and LED lighting.

ORMOCER®s

Inorganic-organic hybrid polymers (ORMOCER®s) have been developed by the Fraunhofer Institute for Silicate Research ISC for over 20 years now. The basic synthetic principle is a combination of modified and controlled sol-gel reactions of organoalkoxysilanes, which result in ORMOCER® resins [HAA00]. Subsequent thermal or photochemical curing of the organic moieties within the ORMOCER® basic structure leads to coatings, particles and bulk materials. The specific know-how of Fraunhofer ISC is based on the complex synthetic process control, which directly influences the material properties on a molecular level, as well as the processing and formulation of the resulting resins to adapt them to the final application. The vast number of combinations of organoalkoxysilanes and transition metal precursors results in the broad range of applications and ready-to-market products, such as scratch-resistant coatings, dental applications and micro-optical or electronic device components [HAA00, SAN05].

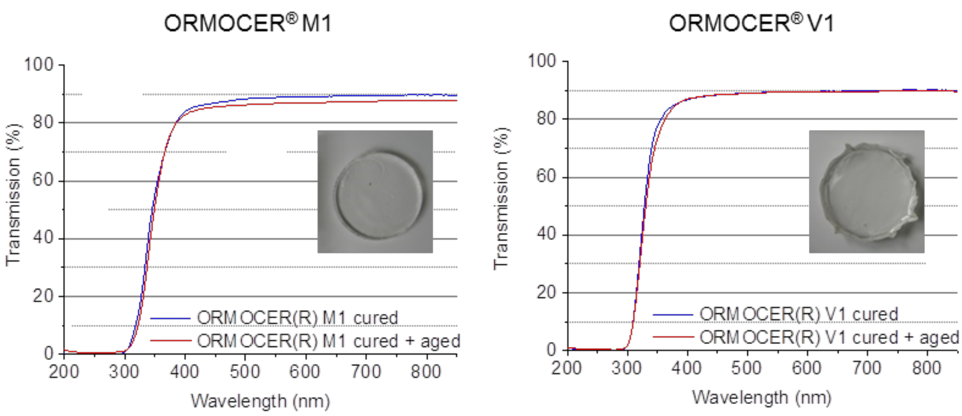
By careful selection of the precursors, the material properties can be tuned. Due to the combination of inorganic and organic moieties on a molecular level, which are bound by strong covalent bonds, the advantages of both materials classes are combined and new synergistic effects are observed [SAN05]. ORMOCER®s exhibit structural elements and properties of ceramics, glasses, organic polymers and silicones and typical properties of these material classes, such as moderate processing temperatures (organic polymers) and chemical and thermal stability (glasses) are combined [HAA00].

Figure 2
Structural elements of ORMOCER®s.



The combination of chemical and thermal stability and broad variety of functional groups is especially advantageous for LED encapsulation and light extraction in general. Organoalkoxysilanes comprising aromatic functional groups can be incorporated within the ORMOCER® structure and lead to increased refractive index accompanied with high thermal and optical stability. Thus, high refractive index ORMOCER®s are promising alternatives to silicones, which often lack the combination of optical stability and high refractive index. A Successful selection of aromatic and polymerizable precursors accompanied with careful optimization of stoichiometry and reaction parameters led to the development of high-index ORMOCER® materials with excellent stability against thermal and irradiation ageing. Figure 3 shows examples of thick film ORMOCER® coatings before and after ageing.

Figure 3
Transmission spectra of ORMOCER® samples (1 mm thickness) before and after ageing (72 h at 150 °C + irradiation (455 nm, 450 mW/cm2)).



The refractive index of these ORMOCER® materials as well as transmission values at 400 nm before and after curing (72 h/150 °C/455 nm) are shown in Table 1. ORMOCER® materials M1 and V1 exhibit excellent properties with respect to thick film stability, refractive index, transparency and aging under simultaneous heating and irradiation.

ORMOCER®	n_D@589 nm (resin)	n_D@635 nm (cured)	%T@400 nm (cured, 1 mm)	%T@400 nm (stressed, 1 mm)
M1	1.568	1.583	87.0	85.6
V1	1.579	1.597	88.5	88.5

Table 1:
Refractive index of resins and cured ORMOCER® films (1mm thickness) and transmission values at 400 nm of cured ORMOCER® films before and after ageing (72 h at 150 °C + irradiation (455 nm, 450 mW/cm2)).

The basic concept in this paper is the combination of ZrO_2 nanocrystals and ORMOCER®s to create high index materials with high thermal and optical stability. The ORMOCER® materials provide improved thermal and irradiation stability in combination with high refractive index, a combination which is often hard to obtain with respect to commercial silicone materials. The use of a stable high index matrix could lead to the same refractive index as typical composites while needing a lower amount of nanocrystal-loading to obtain the same refractive index. Thinking forward, the same or similar loadings might even lead to composites with even higher refractive index. Additionally, further ORMOCER® resins without aromatic groups were tested according their compatibility with ZrO_2 nanocrystals.

Compatibility of high index - ORMOCER®s with ZrO_2 nanocrystals

Different Pixelligent's ZrO_2 nanocrystals dispersed in PGMEA were mixed with ORMOCER® resins to analyze compatibility as well as the resulting refractive indices of these solutions. Figure 4 summarizes exemplary different loadings of PC18-50-PGA nanocrystals in ORMOCER® V1 resins.

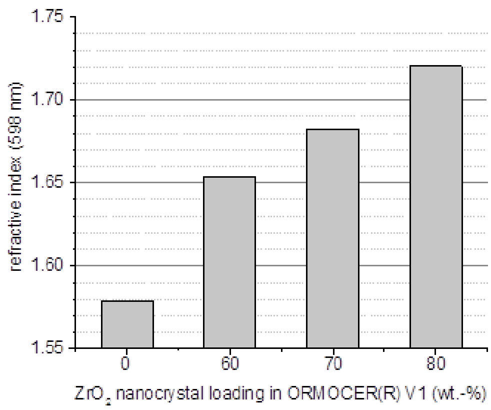


Figure 4
Refractive index (@598 nm) of different loadings of PC18-50-PA in ORMOCER® V1 resin.

The basic refractive index of the pure ORMOCER® V1 resin was increased from 1.579 nm to 1.653 by 60 wt.-% ZrO_2 loading, to 1.681 by 70 wt.-% ZrO_2 loading and to 1.723 nm by 80 wt.-% ZrO_2 loading, respectively, thus showing an increase of 4.7, 6.5 and 9.1 %, respectively. Thus, the combination of Pixelligent's ZrO_2 nanocrystals and ORMOCER® resins proofed to be very promising with high refractive indices of the composite solutions. Careful curing conditions led to transparent composite coatings from different ZrO_2-ORMOCER® mixtures. The reliability and stability against simultaneous aging under temperature and irradiation was measured using visual inspection and UV-vis spectroscopy.

Figure 5

Refractive Indices and UV-vis transmission spectra of cured coatings made of pure ORMOCER® V1b and composite of 40 wt.-% ZrO2 nanocrystals in ORMOCER® V1b, respectively.

Refractive index (matrix)	1.585@635nm
Particle content	40 wt.-%
Refractive index (composite)	1.635@635nm

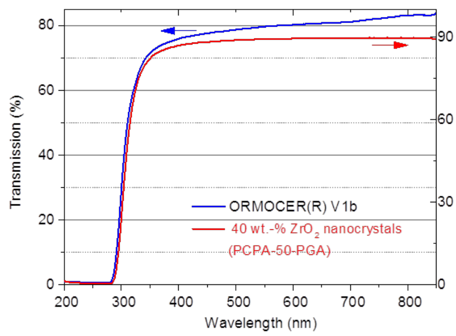


Figure 5 shows a combination of PCPA-50-PGA and ORMOCER® V1. The cured film with a film thickness of about 200 µm contained about 40 wt.-% of ZrO_2 nanocrystals. This inorganic loading led to an increase in refractive index from 1.585 (@635 nm) to 1.635 (@635 nm).

As can be seen from Figure 5, the transmission properties of the pure ORMOCER® V1b was not significantly changed after addition of 40 wt.-% of ZrO_2 nanocrystals and subsequent curing regarding the absorption onset at low wavelengths. The difference in transmission for wavelength of 400 – 800 nm is attributed to slightly different film thicknesses between the pure ORMOCER® (scale on the right) and the composite thin-films (scale on the left). Thus, the composites of PGMEA-dispersed ZrO_2 nanocrystals and high refractive index ORMOCER® show compatibility as well as stability under curing conditions and represent a new promising combination for high refractive index materials.

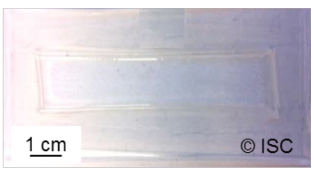
Compatibility of aromatic-free ORMOCER®s with ZrO_2 nanocrystals

Homogeneous, transparent composites with xylene-dispersed ZrO_2 nanocrystals were furthermore prepared with aromatic free ORMOCER®s, demonstrating good compatibility. Figure 6 shows the refractive index of cured composite with different xylene-ZrO_2 nanocrystals in aromatic-free ORMOCER® L.

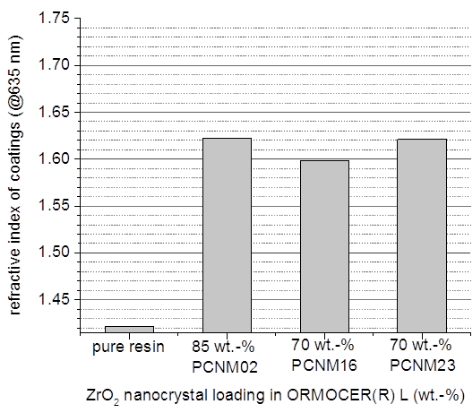
The basic refractive index of the pure ORMOCER® L resin was increased from 1.422 to 1.622 nm by 85 wt.-% ZrO_2 loading (PCNM02), to 1.5891 by 70 wt.-% ZrO_2 loading (PCNM16) and to 1.621 nm by 70 wt.-% ZrO_2 loading (PCNM23), respectively, thus showing an increase of 14.1, 11.7 and 13.9 %, respectively. Approximately twice the amount of ZrO_2 nanocrystals is needed to obtain similar refractive index when using the aromatic free ORMOCER® compared to the previously mentioned high index ORMOCER®s M or V due to the lack of aromatic groups within the resin.

Figure 6

Refractive index of cured composite films (400 µm) of xylene-dispersed ZrO_2 nanocrystals and aromatic-free ORMOCER® L at 635 nm.



70 wt.-% PCNM-16 in ORMOCER® L



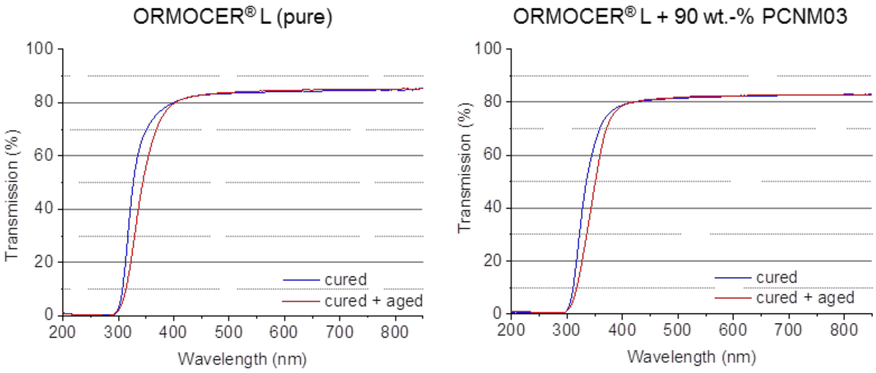


Figure 7
Transmission spectra of ORMOCER® samples (400 µm thickness) before and after ageing (72 h at 150 °C + irradiation (455 nm, 450 mW/cm²)).

Nevertheless, a good compatibility of nanocrystals solutions and resins were observed and transparent, clear composite films were obtained after curing. The stability against aging under temperature and irradiation was evaluated.

Figure 7 shows the UV-vis spectra of the pure aromatic-free ORMOCER® as well as of a composite with 90 wt.-% ZrO_2 nanocrystals.

Only minor changes can be observed in both samples after aging, the pure cured ORMOCER® L and the composite containing 90 wt.-% ZrO_2 nanocrystals. The effect is attributed to minor impurities of the used organosiloxane precursors. Nevertheless, the transmission spectrum of the composite, containing very high nanocrystal loading, exhibits no aging effects which can be traced back to the combination of ORMOCER® and nanocrystals, thus providing a promising alternative to previously investigated composite materials.

Outlook

In summary, promising new combinations for high index composites were found when inorganic-organic hybrid polymers (ORMOCER®s) were combined with Pixelligent's ZrO_2 nanocrystals. The refractive index of mixed solutions and cured thin-films were increased by up to 14 % for the low refractive index, aromatic-free ORMOCER® and 9 % for the high refractive index, aromatic ORMOCER® respectively.

The transmission changes against temperature and irradiation were evaluated for several cured films and showed promising stability, thus providing new candidates in the fields of high-index films such as displays, lighting or ITO index matching. Furthermore, this concept of inorganic-organic matrix materials and inorganic nanocrystals might also be promising in further applications. One example might be tuning dielectric properties such as permittivity of thin-films using these composites.

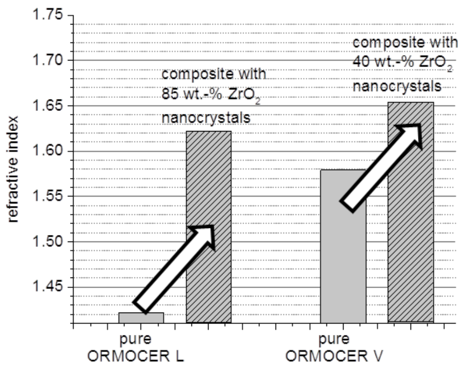


Figure 8
Refractive index change of aromatic-free ORMOCER® L and aromatic ORMOCER® V before and after addition of different amounts of ZrO_2 nanocrystals.