Optical materials and processes for the 21st century

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Photonics, the science of light generation, detection, and manipulation is a ubiquitous technology, which is indispensable for several aspects of today's life: Optical fibers enable fast and reliable intercontinental data transfer, LCD and OLED screens represent a key component for human-machine interaction, and photovoltaic plants harness the energy of the sun for a significant reduction in CO_2 emissions, just to mention a few. Future applications of photonics might involve e.g. the solar-powered generation of fuels (light-to-fuel), optical computing, and automated laser-based manufacturing of individualized goods. Consequently, as the 20th century is considered as the century of the electron, the 21st century might become the century of the photon. While tremendous advances in the manufacturing and miniaturization capabilities of the semiconductor industry along with its scale effects mainly drove the rise of electronics, a similar development can only partially be forecasted for photonics. The large-scale manufacturing of photovoltaic modules and semiconductor laser diodes are success stories that clearly demonstrate the revolutionizing potential of mass production for photonic components. On the other hand, one can assume that only a small quantity of the application potential of photonics has already been leveraged. Among the several reasons that impede a full adoption of photonic technologies, are the difficulties in the assembly of optical systems with narrow tolerances, a lack of standardization, and demanding requirements for optical materials and their processing. The latter means, in particular, highly sophisticated emitters, dies, polymers, coating materials and manufacturing technologies that are fit for of large-scale microfabrication. Fraunhofer ISC as a part of the Fraunhofer Gesellschaft – the largest society for applied research in Europe – is dedicated to promote photonics with unique technology solutions. This article will give a brief overview of activities in the fields of (micro)displays, printed optics and microoptics, which all rely on tailored hybrid-polymers, so called ORMOCER®s.

Several current and future applications of photonics require polymers due to their processing opportunities, i.e. molding, coating, curing, and their price. However, the optical quality and the reliability of conventional polymers are not satisfying in many scenarios. Hybrid polymers, on the other hand, combine the favorable properties of glasses with the processing technology of polymers. Their synthesis is based on a sol-gel like approach, which utilizes different kinds of alkoxysilane precursors. During the synthesis, they form the inorganic (“glass-like”) $[\mathrm{Si\text{-}O}]_n$ network, which is responsible for high thermal and mechanical stability. Si atoms can be partially replaced by heteroelements, such as Zr, to further influence physico-chemical properties of the hybrid polymer. Attached to the inorganic network are organic side groups, which represent a further functionalization of the resin. While a portion of different organic moieties can be utilized to tailor the properties of hybrid polymers, the most important class of moieties are crosslinkable groups, such as (meth)acrylates, epoxides, or styrenes. During the processing, which can be triggered either photochemically or thermally, these groups are polymerized to an additional organic network which leads to a solidification of the resin. Table 1 summarizes the most relevant properties for optical applications.

Refractive index	1.44 - 1.60
Optical absorption	Transparent in the VIS and tailorable towards specific wavelengths in the NIR regime; e.g. @830 nm: < 0.05 dB/cm; @1310 nm: < 0.14 dB/cm; @1550 nm: < 0.26 dB/cm
Mechanical properties	Between < 1 MPa and 1 GPa
Coefficient of thermal expansion	60 – 250 x 10^{-6} / K
Temperature of degradation	Up to 400 °C; Typical: 200 °C
Water uptake	< 0.5 %
Processing technology	UV-lithography, nanoimprint, dispensing, doctor blading, spraying, laser-induced polymerization (one or two-photon)
Additional properties	• Biocompatible and/or biodegradable • Low/no yellowing • Formulation with nanoparticles possible

Table 1: Summary of specific properties for hybrid polymers synthesized at Fraunhofer ISC.

It is obvious from Table 1 that many properties can be tailored to meet application specific requirements. This can be accomplished by the choice of precursors, by varying the synthesis conditions, by the choice of additives (e.g. photoinitiators), and by the processing conditions. A special property of hybrid polymers for optical applications is low yellowing. This is depicted exemplarily in Figure 1 for a high refractive index hybrid polymer. The printed and cured material was exposed to 500 mW/cm² of UV light and 150 °C for 72 hours. The black lines represent the transmission (square) and haze (triangle) before this treatment, whereas the grey lines indicate the status after the experiment. The difference in haze and in transmission is negligible, which renders this material an ideal candidate for long-term operation under harsh conditions.

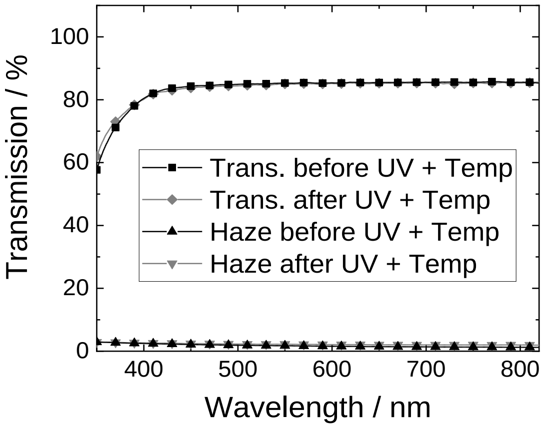

Figure 1: Transmission and haze of a hybrid polymer sample before and after simultaneous temperature and UV-light exposure.

Table 1 already indicates that hybrid polymers can be formulated with nanoparticles (NPs) to extend their spectrum of properties. Typical examples are the incorporation of ZrO_2 nanoparticles for increasing the refractive index or silica nanoparticles to adjust the surface roughness of processed polymer layers. With respect to future applications, the formulation of hybrid polymers with quantum dots (QDs) is of high interest, as the resulting nanocomposite, i.e. hybrid polymer matrix + QD-NPs, has wavelength conversion properties that can be utilized in optical sensing or in displays.

Hence, Fraunhofer ISC developed printable ORMOCER®-based QD-nanocomposites, which do not only exhibit relevant spectral properties of the quantum dots but also excel with the unique durability of ORMOCER®s. Figure 2 illustrates the resulting resin with different kinds of QDs and cured discs under UV illumination.

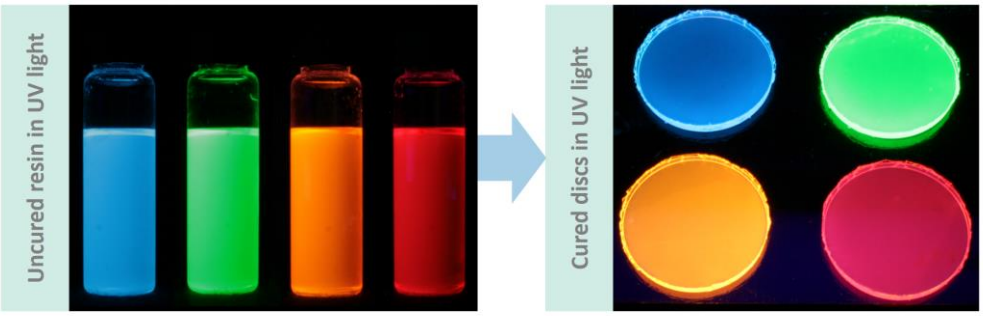

Figure 2: Development of QD hybrid polymer nanocomposites: Quality of dispersion for different ratios of precursors (left). Resin and cured discs with different QD colors under UV light (right).

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The developed nanocomposites are ready for processing with conventional methods like UV-lithography, dispensing and 3D printing by stereolithography. A modification towards low viscosity inks that can be employed in (3D)-inkjet printing, e.g. for QD-displays is envisaged for the near future.

Besides novel high performance materials, the second necessity for a success story of photonics in the 21st century is sophisticated processing technology, which enables high-throughput, high-precision and flexible manufacturing from the micron to the macro scale. A promising manufacturing technology for future applications is two-photon polymerization (2PP) that can be regarded as 3D printing of micron-sized objects. 2PP can generate almost arbitrary 3D microstructures with feature sizes down to 100 nm at any position on almost any kind of substrate (even curved surfaces are possible). An example is given in Figure 3. The left-hand side shows a custom arrangement of 10.000 microprisms on a glass substrate. These prisms form the institute's emblem and refract the blue-light illumination into the observer's eye. Hence, such micro-arrangements act as light-outcoupling or redistribution layers that can be employed in a variety of applications, such as microdisplays for AR and VR. The right-hand side of Figure 3 depicts a 3D demonstrator structure made from the QD-nanocomposites described above. The high fidelity of the patterning process with a wall thickness in the micron range is clearly apparent. 3D micropatterning of these materials using 2PP might gain significant relevance also for display applications, for sensing (when e.g. directly fabricated on active sensor pixels) and in any scenario, that requires microoptical elements with wavelength conversion properties.

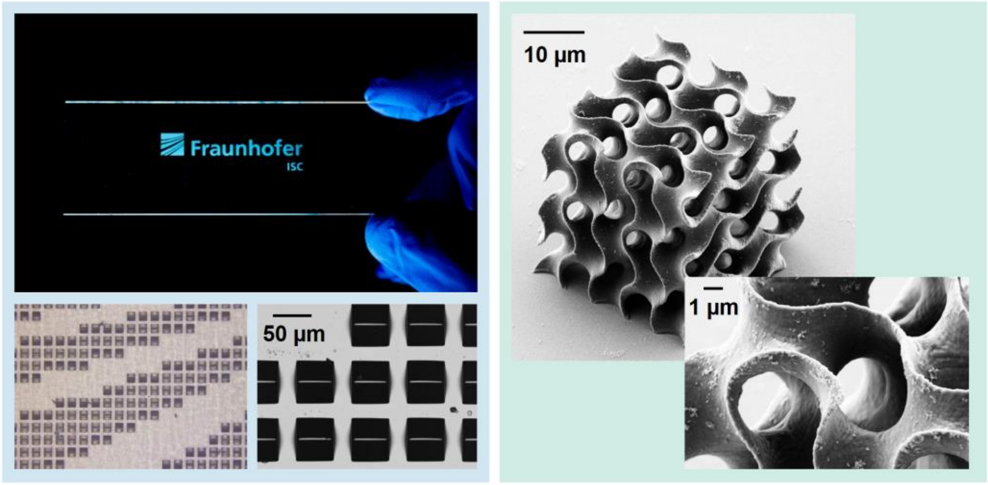

Figure 3: Demonstration of 2PP-written microoptics. Fraunhofer ISC emblem consisting of 10.000 microprisms as light steering device (left). 3D gyroid as a demonstrator for micro-objects fabricated from QD containing composite.

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The micropatterning capability in 2PP stems from an exposure of the (hybrid polymer) resin by ultrafast (here: 350 fs) laser pulses. These visible (515 nm) pulses are tightly focused into the commonly transparent resin leading to extremely high focal intensities. This enables the simultaneous absorption of two photons inside the focal volume, thus triggering the same photochemistry as in UV exposure. Hence, the solidification of the hybrid polymer is strongly confined and a rasterized exposure strategy, as in 3D-printing, and a subsequent removal of the unexposed still liquid resin leads to 3D microstructures.

2PP offers tremendous potential for any application that requires microoptical components, such as multi-level diffractive optics, custom-aspheric microlens arrays, or waveguide structures. Apart from the above-mentioned scenarios in display and sensors this can particularly include projection optics, optical interconnects and – more generally speaking - optical integration. The serial or "point-to-point" nature of the exposure strategy in 2PP renders this technology comparatively slow. Typical durations to generate e.g. a microlens vary strongly, depending on the employed exposure strategy and the utilized positioning velocity of the focal volume. A typical enabler for large-scale manufacturing is the replication of 2PP-written 2.5-dimensional components.

This process including 2PP master-fabrication, stamp/mold making and replication has been successfully demonstrated by Fraunhofer ISC.

Finally, a significant domain of photonics in terms of processing and application is 3D-printed optics. This is considered the "holy grail" in the manufacturing of optical elements as in principle any surface shape - generating arbitrary light distributions - can be manufactured without the need for expensive tools and the time for their fabrication. However, printed optics still suffers from a row of technology inherent hurdles that range from poor property profiles of the employed resins or inks to process-specific artifacts, such as inter-layer boundaries and surface artifacts due to the digital nature of the printing process. Fraunhofer ISC, together with Fraunhofer IOF and Hochschule Aalen, have made a major leap in printed optics in recent years. This has been achieved by a thorough development of printable and solvent free hybrid polymer inks and an optimization of the printing process. Typical results, which showcase the optimization of the surface to be smooth and accurate as well as the volume to be highly transparent and free from impurities can be seen in Figure 4. Typical figures of merit are transparency > 90 % (@400 nm) for 2 mm thickness, average surface accuracy (peak to valley) < 25 µm, and a roughness < 100 nm.

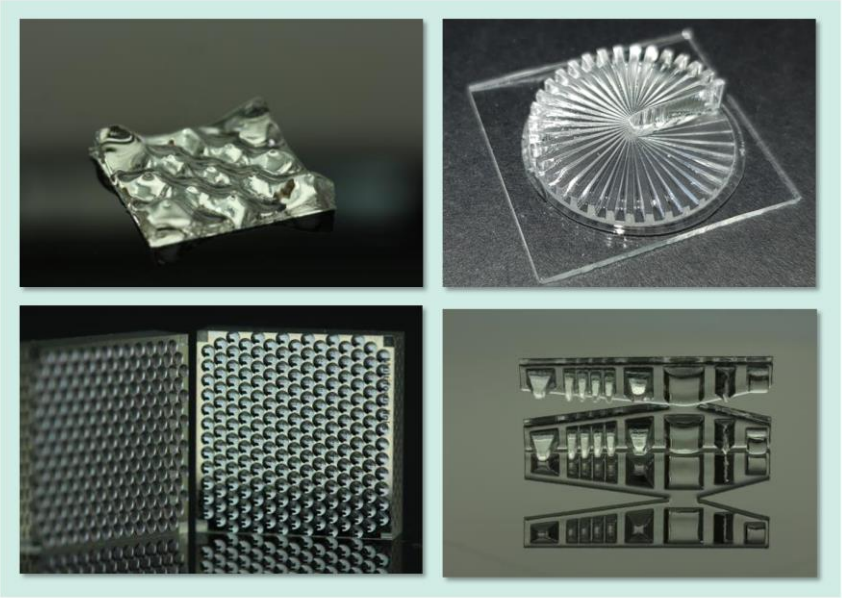

Figure 4: 3D printed components fabricated from hybrid polymers: Top left: Freeform projector (inkjet printing); Top right: 3D Siemens Star (DLP-SLA); Bottom left: Microlens array (inkjet printing); Bottom right: Lightguide for LED (inkjet printing).

The benefit of 3D printing optical components is not only the freedom of shape and the "lot-size = 1" capability. Moreover, digital manufacturing of optical components enables the integration of additional functions inside and onto the printed components which elevates the printed component to an optical system. Fraunhofer ISC, IOF, and ILT have demonstrated several additional functions beyond the mere refraction of light by the optical surface. Among them are: Integrated printed silver mirrors with more than 90 % reflectivity; integrated absorber structures, which act as baffles or apertures; additional microoptical structures on the surface of a 3D-printed object; printed conductive wires for the integration of indicator LEDs into the bulk volume; Antireflective coatings. These additional functions facilitate the assembly and integration compared to a system, which was manufactured conventionally, significantly. This has the potential to strongly decrease the weight and the costs for optical systems in the future, while on the other hand increasing the functionality.

In conclusion, this article highlights perspectives for novel materials and processing opportunities that might coin photonics in the 21st century. The demand for high performance polymeric materials in many application scenarios can be met by tailored hybrid polymers and nanoparticle composites, which utilize these polymers as matrices. In particular, the stability against long-term environmental impacts is a key asset of ORMOCER®s, which is of significant relevance for the pervasive adoption of "polymer optics" in the future. In terms of processing, the trend is clearly digital / additive manufacturing of optical micro- and macro components or even systems. 2PP and 3D-printing via inkjet or stereolithography represent extremely flexible processing approaches that are, at current state not yet ready for industrial application, but can be regarded as enablers for future applications, in which the freeform aspect, individualization and functional integration become decisive. Both, material and processes advances, will pave the way to a bright photonic future.

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