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Abstract. Several polymer films for improved optical properties in optoelectronic devices are presented. In such optical applications, it is sometimes important to have a film with an adjusted refractive index, scattering properties, and a low surface roughness. These diffusing films can be used to increase the efficiency of optoelectronic components, such as organic light-emitting diodes. Three different epoxy acrylate mixtures containing Syntholux 291 EA, bisphenol A glycerolate dimethacrylate, and Sartomer SR 348 L are characterized and optimized with different additives. The adjustable refractive index of the material is achieved by chemical doping using 9-vinyl-carbazole. Titanium nanoparticles in the mixtures generate light scattering and increase the refractive index additionally. A high-power stirrer is used to mix and disperse all chemical substances together to a homogenous mixture. The viscosity behavior of the mixtures is an important property for the selection of the production method and, therefore, the viscosity measurement results are presented. After the mixing, the monomer mixture is applied on glass substrates by screen printing. To initiate polymerization, the produced films are irradiated for 10 min with ultraviolet radiation and heat. Transmission measurements of the polymer matrix and roughness measurements complement the characterization. © *2017 Society of Photo-Optical Instrumentation Engineers (SPIE)* [DOI: 10.1117/1.OE.56.3.037105]

1 Introduction

High refractive index polymeric scattering layers are highly interesting for the implementation in (organic) light-emitting diodes (OLEDs) for the use as light extraction layers. In a typical OLED, only about 20% of the light generated in the component is out coupled.[1] The reasons for this are waveguiding and subsequent absorption,[2] which strongly limits the device efficiency.

To improve the fraction of out coupled light, periodic or random micro/nanostructures can be introduced in the layer stack to scatter the waveguide modes or substrate modes.[3,4] Another possibility to increase the light out coupling is lenses on the surface of OLEDs.[5–12] Hollow spheres embedded in the layers[13] or glass substrates blast with sand[14] are other possibilities for scattering the light. However, these methods are very time-consuming or very costly.

This paper is an extension of the SPIE proceeding[15] and describes the development of a polymer scattering layer in which ceramic nanoparticles scatter the light, with the aim of improving the out coupling efficiency of OLEDs. Well-suited polymers are epoxy resins, because they exhibit a refractive index of about 1.56 (589 nm, 20°C).[16] Since the organic layers of the OLED exhibit high refractive indices of around 1.8, the scattering layer's refractive index should be close to this value to maintain a high mode overlap and, therefore, better waveguide mode extraction.[2] To obtain the conditions required to increase the refractive index, the polymers are combined with aromatic compounds possessing a large number of π-electrons.[17]

The white ceramic TiO_2 nanopowder serves not only to scatter light, but also increase the refractive index of the layers.[18]

2 Materials

In this work, three different monomer mixtures are presented. The first mixture contains 80 wt. % Syntholux 291 EA from Synthopol Chemie, and the second mixture contains 80 wt. % bisphenol A glycerolate dimethacrylate from Sigma-Aldrich. The last mixture includes 80 wt. % Sartomer SR348 L from the Sartomer Arkema Group. The reactive monomers or monomer/polymer mixtures based on bisphenol A are referred as epoxide-based polymers since they are prepared from bifunctional bisphenol-A-diglycidyl ether.

For better processing, 10 wt. % benzyl methacrylate (96%, BMA) from Sigma-Aldrich is added to lower the viscosity. To improve the hardness, bonding strength, and chemical stability, 10 wt. % cross-linking agent 1,3-butane-diol dimethacrylate (95%, BDDMA) from Sigma-Aldrich is added in the mixture. The added amount is a compromise between low viscosity, chemical stability, and high refractive index. BMA exhibits a refractive index of 1.52 and BDDMA exhibits a very low value of 1.45, hence large amounts should be avoided to maintain a high refractive index of the final mixtures. Light scattering is achieved through the targeted addition of nanoscale titanium dioxide P25 (particle size: $d_{10} = 93$ nm, $d_{50} = 120$ nm, and $d_{90} = 450$ nm[19]) from Evonik Industries. The refractive index of the polymer layer can be increased by the addition of the dopant

9-vinylcarbazole (98%) from Sigma-Aldrich. To initiate the polymerization, diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (98%) from TCI Deutschland GmbH or benzophenone (99%) from Sigma-Aldrich can be used as a ultraviolet (UV) photoinitiator. Lauroyl peroxide (97%) from Sigma-Aldrich is suitable as a thermal initiator in the mixtures. In all mixtures the proportion of UV- and thermal initiator is 3 wt. % and 1 wt. %, respectively, of the total monomer weight. To prevent the particles from agglomeration and sedimentation, [2-(2-methoxyethoxy)ethoxy]acetic acid (90%, TODS) from Clariant is employed in slight amounts as a stabilizer. TODS is a well-suited stabilization agent for ceramic nanoparticle powder and is often used in ceramic slurries to create homogenous stabilized particles.[20] The three mixtures will be characterized in the following sections.

3 Experimental

All chemical components are mixed with a high-performance stirrer (IKA T10 basic Ultra Turrax) for 5 min and treated with a sonifier (Branson Digital W450, 40% power) for 1 min. The rheological characterization then follows with a Bohlin CVO50 rheometer from Malvern Instruments. Here, a cone with a diameter of 40 mm and a gap size of 150 μm is used. The measurements are carried out at three different temperatures, 20°C, 40°C, and 60°C. The shear rate is varied from 10 to 100 s^{-1}.

As the refractive index can only be determined with transparent samples using the Abbe refractometer (DR-M2/1550) from ATAGO, separate samples without titanium dioxide must be prepared. The samples are polymerized in a nitrogen atmosphere; otherwise, the oxygen of the ambient air would
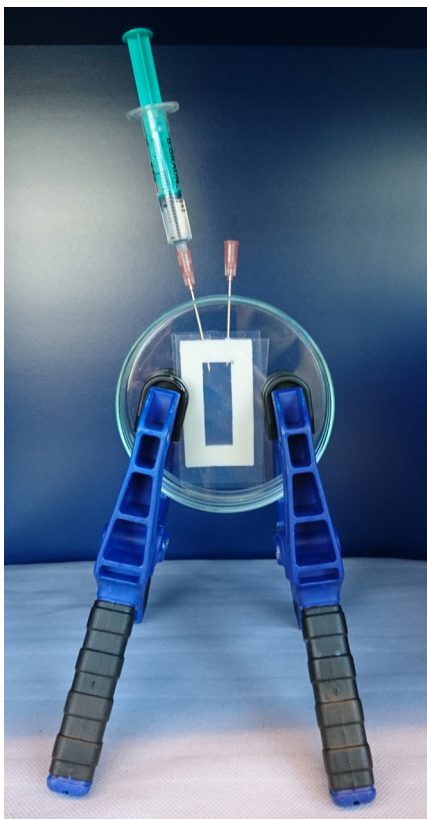
inhibit the polymerization process. When the photoinitiator diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (98%) is used, a UV LED (Hoenle, 405 nm, 1000 mW/cm^2, 10 min) is used, whereas when benzophenone is used as a photoinitiator, a mercury lamp (8 mW/cm^2) is used due to better overlap of emission and absorption spectra. A postcuring treatment at 150°C over a period of 30 min then follows to enhance the degree of polymerization. The refractive index measurements are conducted with an Abbe refractometer at 20°C and 589 nm. For this measurement method, it is necessary to have transparent, flat, bubble-free specimens without TiO$_2$ particles. A special configuration in Fig. 1, which includes two glass plates, tetrafluoroethylene–perfluoropropylene foils, and glue clamps, is used as mentioned in a previous work.[21]

UV–visible (Vis) measurements were performed with a Varian Cary 50 spectrophotometer in the wavelength from 400 to 1100 nm on samples with a thickness of 3 mm.

For the production of scattering layers, a screen printing device K15 Q-SL from the company Kammann (parameters: coating speed = 100 mm/s, angle = 75 deg) is employed. The layer roughness is determined with the aid of a white-light interferometer WLI Sensofar Plu Neox.

4 Results and Discussion

4.1 Flow Properties

The flow properties are important characteristics and are necessary for the rheological matching to the later industrial production process (printing, spraying, or coating). Figures 2 to 4 show the results. The mixtures exhibit Newtonian flow behavior at all temperatures. At higher temperatures, the mixture's viscosity decreases. By comparison, the Sartomer mixture shows the lowest viscosity and the bisphenol A glycerolate dimethacrylate shows the highest viscosity.

### 4.2 Ultraviolet–Visible Measurements

For further characterization of the different epoxy acrylate mixtures, UV–Vis measurements were carried out on the 3-mm-thick polymerized samples. The wavelength range was between 400 to 1100 nm. The reason for the UV–Vis measurement is to analyze the amount of light transmitted through the polymer matrix in the UV and Vis range. The results are illustrated in Fig. 5 and show that the samples exhibit a transmission of about 80% in the wavelength range from 450 to 1100 nm. In some other publication, the films show a higher transparency of 92% at a wavelength of 520 nm, but the thickness of their samples is 1.4 μm.[22] With consideration of the Beer–Lambert law, we present comparable light transmittance values.

4.3 Refractive Index Measurements

9-Vinylcarbazole increases the refractive index of the polymer matrix in cured samples. It was found that the solubility of this powder is especially high in the mixtures. Up to 40 wt. % vinylcarbazole could be dissolved in the Syntholux and Sartomer mixtures. In bisphenol A glycerolate dimethacrylate mixtures, a solubility of up to 30 wt. % was obtained. The good solubility of vinylcarbazole enables the realization of a high refractive index of up to 1.625 at 20°C and 589 nm by the Sartomer and Syntholux mixtures. Figure 6 shows the

Fig. 1 Construction for specimen production.
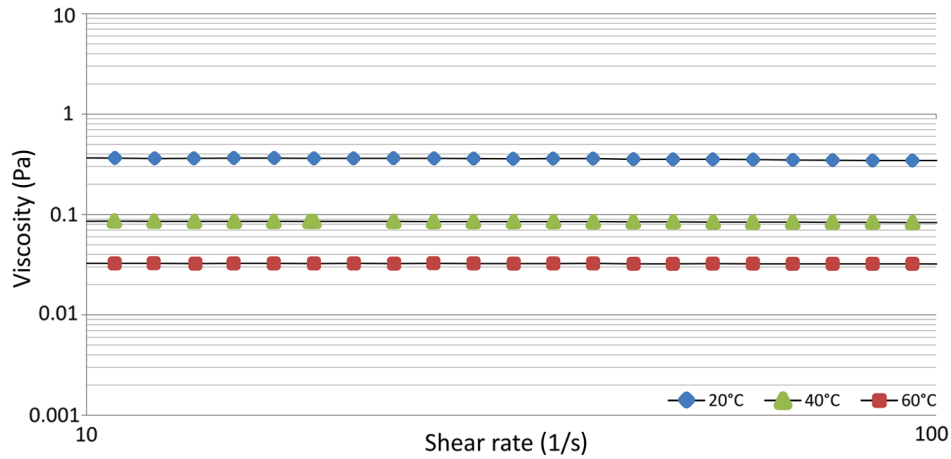
Fig. 2 Viscosity behavior of the Sartomer basic mixture (80 wt. % Sartomer, 10 wt. % BMA, and 10 wt. % BDDMA) by variation of the shear rate and three different temperatures.
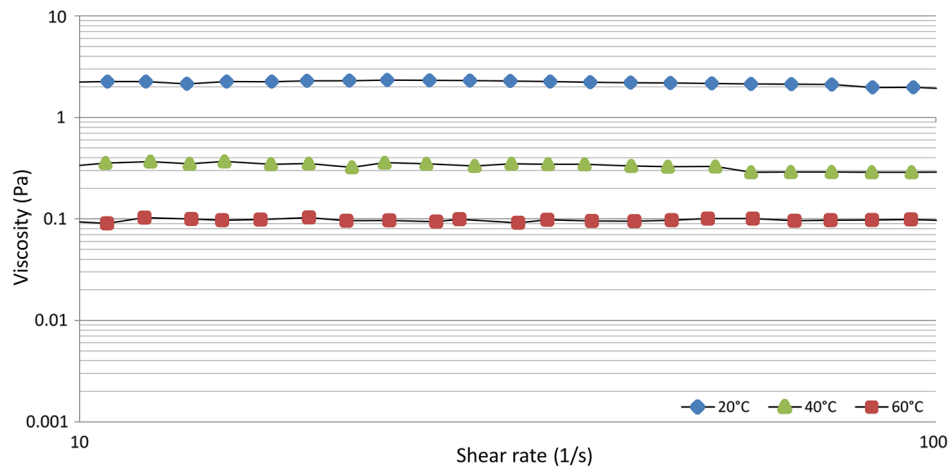
Fig. 3 Viscosity behavior of the Syntholux basic mixture (80 wt. % Syntholux, 10 wt. % BMA, and 10 wt. % BDDMA) by variation of the shear rate and three temperatures.
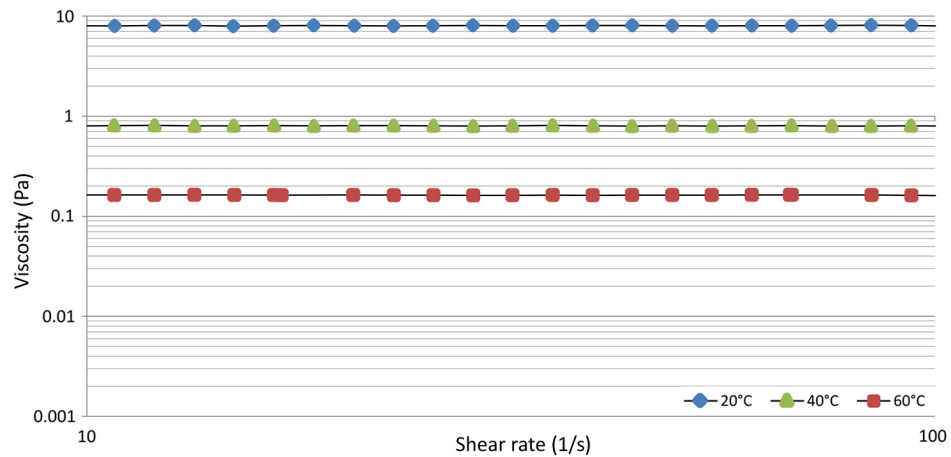
Fig. 4 Viscosity behavior of the bisphenol A glycerolate dimethacrylate basic mixture (80 wt. % bisphenol A Gly., 10 wt. % BMA, and 10 wt. % BDDMA) by variation of the shear rate and three temperatures.

results of the Abbe refractometer measurements at 20°C and 589 nm. Other research groups present a lower refractive index for their polymer matrix consisting of a transparent photoresist in the range between 1.52 and 1.54 (450 to 650 nm).[22]

4.4 Roughness Measurements and Transmittance of the Scattering Layer

A smooth surface of the scattering layer is important, because inhomogeneities, such as particle agglomeration,
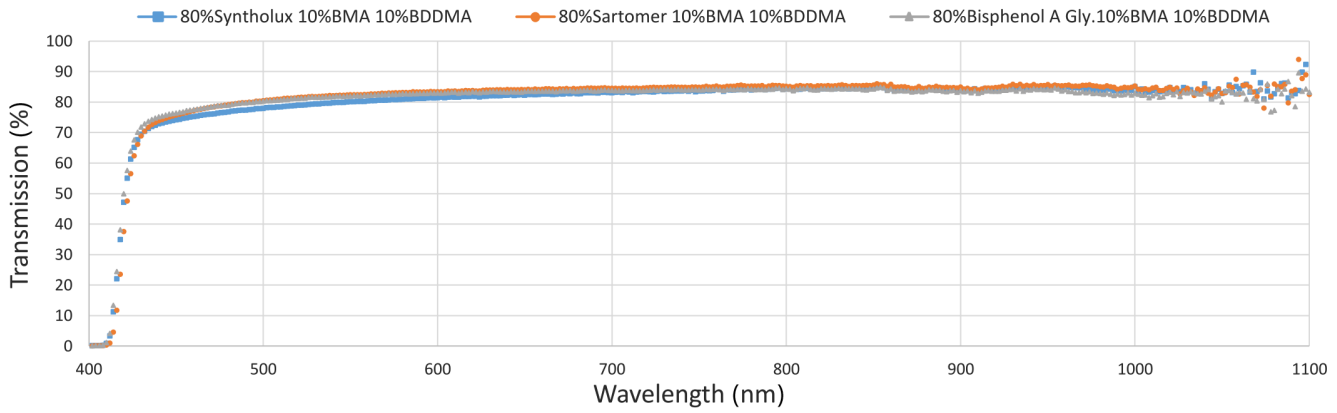
Fig. 5 UV–Vis measurements from 3-mm-thick polymerize samples from the three basic mixtures.
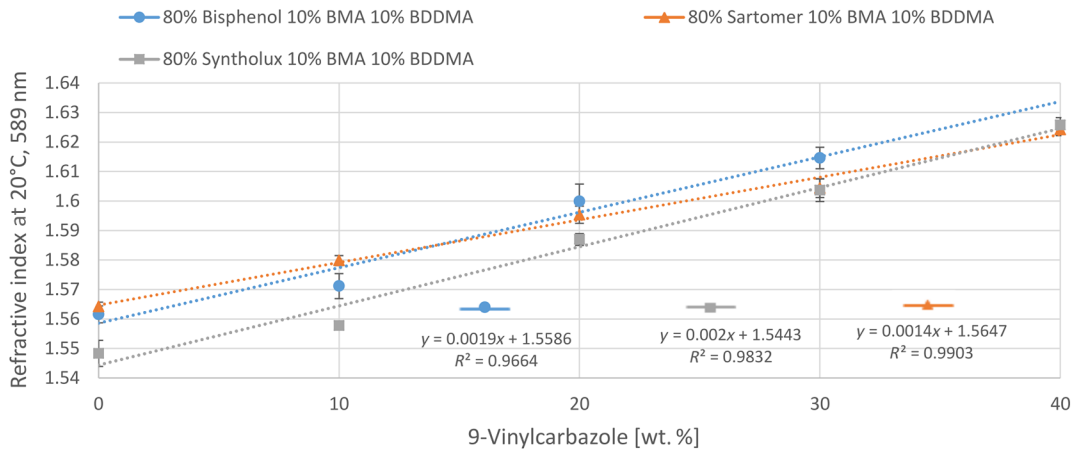

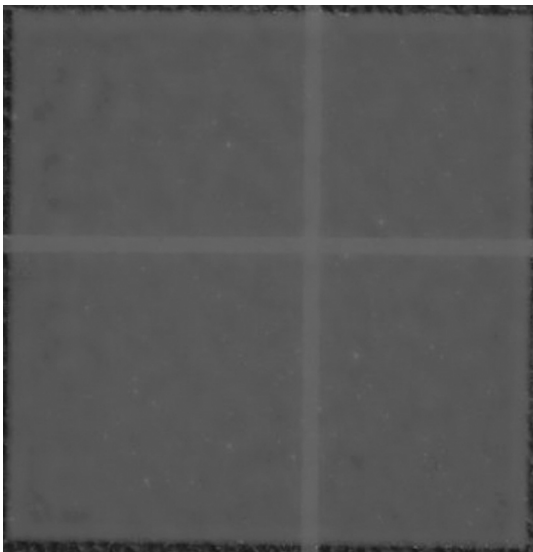**Fig. 6** Refractive index measurements (20°C, 589 nm) with increasing amount of 9-vinylcarbazole.

Fig. 7 Picture of a scattering layer screen printed on a glass substrate.

Table 1 Roughness values of a screen-printed sample after polymerization

Sample number	Spot size 127.32 × 95.45 μm^2		Thickness of layer
	Ra (nm)	rms (nm)	d (μm)
1	69.3	88.0	13.9
2	51.5	62.2	10.1
3	76.8	98.4	14.8

can lead to electrical defects in the OLED stack. Figure 7 presents our best result from a scattering layer on a glass substrate. The roughness values of the sample are below 100 nm (rms). Table 1 gives the roughness values of a scattering layer comprised of 55 wt. % Sartomer mixture, 36 wt. % 9-vinylcarbazole, and 9 wt. % TiO$_2$ P25 + additives produced by screen printing. In Fig. 8, an overall transmittance
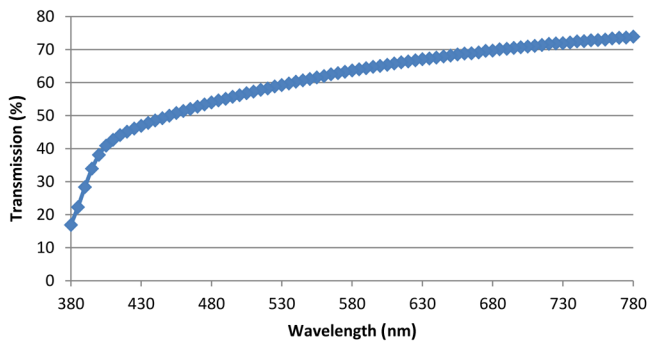
Fig. 8 Transmittance measurement of a scattering layer.

measurement of a scattering layer is presented at a sample thickness of 20 μm. It shows a transmittance between 18% and 75% depending on the wavelength.

5 Summary

In this work, it could be shown that the refractive index can be varied over the range from 1.55 to 1.62 (589 nm, 20°C). The adjustment of the refractive index is regulated by the addition of 9-vinylcarbazole. The lowest viscosity of 0.03 Pa s at 60°C was found for the Sartomer base mixtures and the highest viscosity of 8 Pa s at 20°C shows the bisphenol A mixture. The samples of the basic polymers exhibit a transmission of about 80% in the wavelength range from 450 to 1100 nm. The samples exhibit a roughness less than 100 nm (rms).

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