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Optically and rheologically tailored polymers for applications in integrated optics

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ABSTRACT

We demonstrate an epoxy acrylate based system on which various micro-optical applications can be realized. With this innovative and flexible material concept, it is possible to adjust viscosity (3 mPa s < η < 46 Pa s) as required for different microstructuring processes e.g. inkjet printing, spin coating, and stereolithography and simultaneously precisely tailor refractive indices ($1.518 < n_{D,20} < 1.569$) which is essential to implement optical sensor concepts. The practicability of this material system is demonstrated for optical waveguide production and selected applications. The fast and low cost modification of optical and rheological material properties is advantageous for the fabrication of micro-optical polymer devices including planar-optical polymer sensor networks.

1. Introduction

For polymer based optronic systems, suitable polymer materials with defined physical and chemical properties are strongly needed which then path the way for applications in sensing, signal processing and data transmission [1–7]. Starting in the early 1960s, functional polymers lead to remarkable success in this field, leading to the development of a variety of different properties for applications in photovoltaic devices, LEDs, organic thin films or biomedicine [2,8–10]. They are now widely used in functional films, telecommunication applications, micro-optical components, and optical sensor concepts [6,11–15].

Refractive index is one of the key material parameters which has to be controlled and adjusted in such materials with regard to the realization of optical sensor systems, light sources and detectors or the substrate on which the required waveguides are deposited. Different approaches have so far been shown to modify the refractive index, such as the partially complex inorganic-organic multi-component hybrid materials for optical applications, as reviewed by Carlos et al. [5]. Another approach is the expansion of the polymer matrix with ceramic nano-particles like titanium dioxide. This is, however, difficult because these particles can agglomerate which then leads to an increase in optical damping due to scattering [16–19]. Avoiding huge effort and complex synthesis, the adequate choice of a co-monomer as well as the addition of guest molecules like phenanthrene are a simple and low cost method for refractive index adjustment [20].

With regard to the different production techniques of polymer devices (e.g. waveguide structures, feature sizes down to 10 μm), the viscosity of the material systems from which they are fabricated is a critical factor. Inkjet or offset printing, nanoimprint lithography, and reaction molding are “cold” processing methods where the monomer is shaped before UV-light or thermal induced polymerization is started. These processes have seen an increase in importance for optical waveguide fabrication [7,21,22]. While inkjet printing requires viscosities of around 50–500 mPa s [23], a viscosity around 200 mPa s suffices for offset or flexo printing.

In this work, the influence of the comonomer benzyl methacrylate in combination with Syntholux, a commercially available epoxy methacrylate, on the rheological, optical and thermomechanical properties of the compound material is investigated. This study is based on earlier investigations on the epoxy acrylate system [24],

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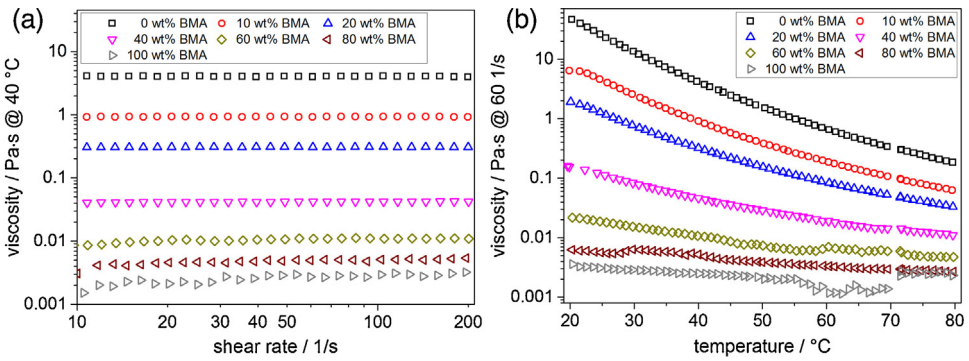

Fig. 1. Viscosity of mixtures of Syntholux and BMA measured with a cone and plate rheometer: (a) shear rate dependent and (b) temperature dependent.

enabling a wider range of applications of this material system in future.

2. Material system and characterization method

2.1. Materials and sample preparation

Three different monomers were used as starting material of the material system developed here. Syntholux, a commercial epoxy methacrylate, was used as main matrix monomer. Viscosity adjustment was done by using a suitable co-monomer. For UV curing a photo initiator was added. All used materials and their function are shown in Table 1.

The materials were mixed with a high speed stirrer (Ultra-Turrax T10, IKA, Staufen, Germany) under ambient conditions until a homogenous mixture was obtained. Polymerized samples made out of the different mixtures were produced for refractive index, optical damping and glass transition temperature measurements. For this, a setup made from glass plates, a silicone casting mold and FEP (fluorinated ethylene propylene)-foils was used. Polymerization was performed using a wavelength of 405 nm.

2.2. Characterization

The viscosity of the material system was determined by two distinct experiments with a cone and plate rheometer (CV50, Bohlin, Herrenberg, Germany). The first measurements were taken at a constant shear rate of 100 s^{-1} over a temperature range between 20 and 80 °C. Following this, the shear rate was swept logarithmically from 10 s^{-1} to 200 s^{-1} at temperatures of 20 °C, 60 °C and 80 °C. For quantification of refractive indices, an Abbe refractometer (DR-M2/1550, Atago, Tokyo, Japan) set at a temperature of 20 °C was used at three different wavelengths (450, 589, and 680 nm). Abbe numbers were then calculated. Optical damping values of the polymerized samples and materials, respectively, were obtained by gathering data with a UV–vis spectrophotometer (Cary 50 UV–vis, Varian, Waldbronn, Germany). This data was normalized by the sample thickness and corrected by the reflection losses occurring at the two interfaces of the sample and the surrounding air. The glass transition temperature (T_g) of polymerized samples was measured under nitrogen atmosphere using differential scanning calorimetry (DSC) (Phoenix 204F1, Netzsch, Selb, Germany). The temperature was increased from -80 °C to 200 °C with a heating rate of 10 K/min.

3. Results and discussion

3.1. Material fabrication

3.1.1. Flow behavior

The evaluation of the viscosity measurements shows a Newtonian behavior (shear rate independent) for all mixtures, as seen in Fig 1 (a) and for all investigated temperatures. On the other hand, the viscosity was found to be strongly influenced by temperature and BMA content as it is shown in Fig. 1 (b). At 20 °C, pure Syntholux shows a high viscosity of 46 Pa s which decreases to 0.18 Pa s at 80 °C. Pure BMA, conversely, shows a fairly low viscosity of 3.5 mPa s at 20 °C, which is clearly measured at the limit of the rheometer sensitivity range. BMA content dependence of the system can be also seen with a viscosity of 26 Pa s at 25 °C for pure Syntholux which decreases down to 3.1 mPa s for pure BMA. This data clearly shows that the material system can be adjusted to the various needs of the different microstructuring methods like inkjet or offset printing.

3.1.2. Optical and thermomechanical properties

The refractive index of the analyzed material system increased linearly with increasing BMA content, starting at $n_{D,20} = 1.550$ for pure Syntholux and reaching $n_{D,20} = 1.569$ for pure BMA (Fig. 2 (a)). Based on this data, the refractive index can be adjusted with high accuracy. Deviations in measured values are a result of sample fabrication and measurement principle. Air bubbles or dust in the sample or between sample and main prism of the Abbe refractometer can compromise measurement results [25]. Abbe numbers which were then calculated from the refractive index data are around 35 and are not influenced by BMA (Fig. 2 (b)). Optical damping of the polymerized samples strongly correlates with BMA. Samples out of pure Syntholux show a damping of 3 dB/cm at 600 nm which decreases to 0.5 db/cm for samples containing 80 wt% BMA (Fig. 2 (c)).

Merging the viscosity and refractive index data of the presented material system, a clear dependence of refractive index on viscosity can be seen and is shown in Fig 3. The same is done for the data of the material system presented earlier consisting of Syntholux and EGDMA [24]. With this co-monomer, the refractive index, in contrast to the case with BMA, linearly decreases with increasing co-monomer content. A total change in refractive index of up to 0.05 is possible, reaching a maximum of $n_{max} = 1.568$ and a minimum of $n_{min} = 1.518$ with the respective co-monomer, while still maintaining the same viscosity. With these combined material systems, for processes where viscosity is critical, it is now to realize optical waveguides where core and cladding require different refractive indices while viscosity must be constant.

For the potential applications of the material system, for example in optical sensor networks, the continuous operating temperature is of great importance. This temperature is somewhat lower than the glass transition temperature, and for a short period of time and without external stress the material can also be used at slightly higher temperatures. There are three points, which can be calculated for the glass transition temperature within the Proteus Thermal Analysis Software (Netzsch, Germany). The first and second point are denoted as the midpoint and the onset, respectively, and are determined by the tangent method, whereas the third is the inflection point [26,27]. When looking at the inflection point,