

## NEW UV-CURABLE ADHESIVES WITH VARIABLE REFRACTIVE INDEX BASED ON INORGANIC-ORGANIC NANOCOMPOSITES (NANOMER®) FOR OPTICAL COMPONENTS

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New transparent UV-curable adhesives for the use in integrated optics based on organic-inorganic nanocomposites (NANOMER®) have been developed. These adhesives show excellent optical properties, whereby a high content of SiO<sub>2</sub> particles with an average particle size of 10 nm can be achieved (up to 35 vol-%). The thermal expansion coefficient could be reduced from 75 ppm/K down to 30 ppm/K with a filler content of 20 wt-% (15 vol-%). The refractive index could be varied from 1.450 (cured 1.461) to 1.546 (cured 1.558), at a wavelength of 644 nm, by variation of the synthesis. UV-curing was faster compared to UV-curable commercial epoxy resins.

### 1 INTRODUCTION

Adhesives, used for fabrication of optical components such as fiber-chip couplers or fiber-fiber couplers, have to fulfill several technical requirements. In many cases, the adhesives are a part of the optical path and therefore low internal optical losses, caused by absorbance or scattering, are demanded. Furthermore, adhesives with precisely adjustable refractive index are required in order to minimize coupling losses caused by Fresnel reflection at the interfaces of the joint. For the fabrication of fiber chip couplers and other components, active adjustment is used in many cases. Therefore, rapid UV curable adhesives with low shrinkage are required, which do not show post curing effects, in order to avoid disalignment ( $\pm 0.1 \mu\text{m}$ ) during or after curing [1].

Further requirements are low coefficients of thermal expansion in the temperature range between  $-45^\circ\text{C}$ .... $85^\circ\text{C}$  in order to minimize reversible disalignment, caused by a mismatch of the coefficient of thermal expansion (cte) of the adhesives (about  $10^2$  ppm/K) and the bonding partners (0.5....10 ppm/K). Furthermore, the transformation temperature of the adhesive must not lie inside the working temperature range.

Commercially available UV-curing optical adhesives are based on acrylates, epoxy resins or mixed systems [2]. Acrylates show rapid UV curing by radical polymerization, but their main drawbacks are their low transformation temperature and their high cte [1,3,4]. Epoxy resins exhibit transformation temperatures of  $> 120$  °C and a notably lower cte, but UV curing by anionic polymerization is slower than radical polymerization and thermal post curing cannot be avoided [2]. This hinders high production rates and results in high costs for the assembly of optical components and devices.

Therefore, the aim of this paper was to develop new optical adhesives based on inorganic-organic nanocomposites (NANOMER<sup>®</sup>) with a high content of nanoscaled SiO<sub>2</sub> particles as an inorganic, transparent filler. The approach was to synthesize a matrix with a high degree of Si-O-Si condensation as an inorganic backbone in order to reduce the curing time during the photochemically induced polymerization of the epoxy groups.

## 2 EXPERIMENTAL

GPTS (3-glycidyloxypropyltrimethoxysilane) was chosen to prepare UV-curable adhesives by the sol-gel-process. After hydrolysis and condensation of the silicon alkoxide, followed by the removal of the solvent by distillation and addition of photoinitiators, polymers with a Si-O-Si backbone and UV-curable organic side-chains were obtained.

The inorganic-organic matrices can be filled with nanoscaled SiO<sub>2</sub> particles, which are incorporated by adding an organo-silica sol such as Nissan IPA-ST<sup>®</sup>. To achieve high silica contents and in order to increase the pot life of the filled adhesives, the surface of the silica particles has to be modified using quaternary ammonium salts.

By co-condensation with silicon alkoxides containing alkyl, fluorine or phenyl groups and by mixing with different commercially available epoxy resins, with high refractive index, adhesives with an adjustable refractive index were prepared. A detailed description of the preparation route is given in [5]. The adhesives were cured using a high-pressure mercury UV-Lamp (UVP-200, Panacol-Elosol GmbH) with a UV intensity of 75 mW/cm<sup>2</sup> within 180 seconds.

Shrinkage was evaluated by comparison of the density of the cured (Archimedes method) with the liquid (pycnometer) product. Measurements of the thermal expansion coefficient between -50 °C and 250 °C were performed using a Mettler TMA 40 dilatometer and cured samples of 1 mm thickness. Viscosity was investigated with a Physika UM viscometer (cone/plate MK 20, 50 µm slit, 0...500 s<sup>-1</sup>). Microhardness was determined with a recording Fischerscope H100. DSC (Differential Scanning Calorimetry) measurements

were performed using a Seico DSC 220C differential scanning calorimeter (-50...250 °C, 10 K/min). Bond strength was determined by measurements of the pressure-shear-strength of two float glass plates bonded with the adhesive (size 20 mm x 20 mm, intersection 5 mm) as described in [6]. Refractive indices were determined by the use of an Abbé refractometer (623 nm) in the case of the liquid samples and a Pulfrich refractometer (644 nm) in the case of the cured product.

### 3 RESULTS AND DISCUSSION

UV-curable adhesives were prepared by the sol-gel-process using GPTS and a cationic photoinitiator. In order to tailor the refractive index, different matrix modifications have been investigated. The maximum range of the refractive indices achieved is shown in FIGURE 1.

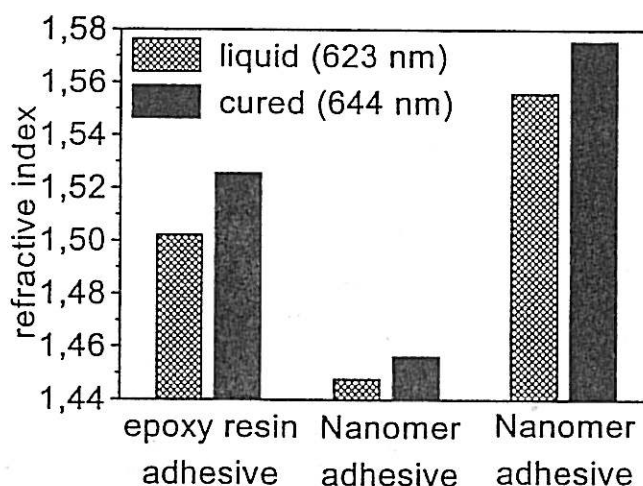


FIGURE 1

Comparison of NANOMER adhesives with low (middle) and high (right) refractive index compared to a commercial epoxy adhesive (left)

By co-condensation of GPTS with alkyltrialkoxysilanes, or alkoxy silanes having fluorinated groups, refractive indices of the cured adhesives could be lowered from about 1.50 down to 1.457 (wavelength 644 nm). Most commercially available UV-curing adhesives have refractive indices in the range of 1.48....1.56 [6,7,8,9]. A few acrylates reach refractive indices of 1.45 [6,9]. A quantitative comparison of the refractive index is not possible, since data are only available for the liquid phase. However, it is obvious from FIGURE 1 that the refractive index increases for the cured adhesive caused by the higher density due to the shrinkage, which is relevant for technical application. High refractive indices up

to 1.567 (644 nm) of the cured adhesive could be achieved by the co-condensation of GPTS with alkoxysilanes containing phenyl groups or by combination of the NANOMER adhesive with high refractive index epoxy resins. For comparison, the data of a commercially available epoxy based adhesive, used in optical industry is included in FIGURE 1 (left). It shows that the refractive index of the Nanomer adhesives can be brought into a range suitable for optical applications.

Due to the nonpolar character of the alkyl- and fluorine groups used for adhesives with low refractive index, the amount of glass bonding Si-OH groups was reduced. Therefore, it was important to investigate the bond strength of the low refractive index Nanomer adhesive. For this investigation, adhesives were also prepared by mixing the commercially available epoxy adhesive (refractive index about 1.5) with the low refractive index Nanomer adhesive (compare FIGURE 1) in various compositions.

FIGURE 2 shows the bond strength of the different compositions, measured by pressure-shear experiments with float glass (average strength and standard deviation of 5 samples at each content).

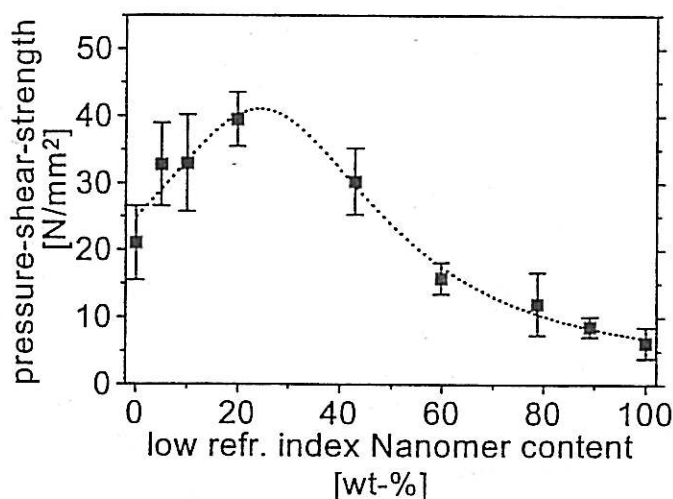


FIGURE 2

Bond strength of a low refraction index NANOMER adhesive in relation to the content of a commercial epoxy adhesive, determined by pressure-shear-experiments

As shown in FIGURE 2, bond strength of the epoxy resin based adhesive increases strongly with increasing Nanomer content, reaching a maximum of about 40 N/mm<sup>2</sup> for a Nanomer content of 20....30 wt % before decreasing down to 10 N/mm<sup>2</sup> for the pure low refraction index Nanomer adhesive. In all cases adhesion failure was obtained. The interpretation of this figure is difficult as the composition of the epoxy adhesive is not

known. But it might be assumed that the increase of the bond strength for low Nanomer contents is due to the increasing number of Si-OH groups in the adhesive. Furthermore, it may be assumed that for higher Nanomer contents the flexibility of the adhesive decreases, which promotes adhesion failure. This hypothesis has to be proven by further investigations, but the obtained bond strengths are sufficient for applications in fiber-chip-coupling, where a limit of 10 N/mm<sup>2</sup> is demanded [10]. For the further discussion of the properties of Nanomer adhesives, a formulation with a refractive index comparable to the commercial adhesive was chosen, which showed the highest bond strength.

In the next step of the development, the incorporation of nanosized SiO<sub>2</sub> filler particles into the Nanomer adhesive was investigated in order to reduce the cte of the Nanomer adhesive (appropriate results for the commercially available epoxy resin based adhesive are presented in [11]). For this reason the incorporation of colloidal SiO<sub>2</sub> particles in isopropanol was investigated, as described in [5], and the viscosity of the filled uncured adhesive was measured as a function of filler content. FIGURE 3 presents the results.

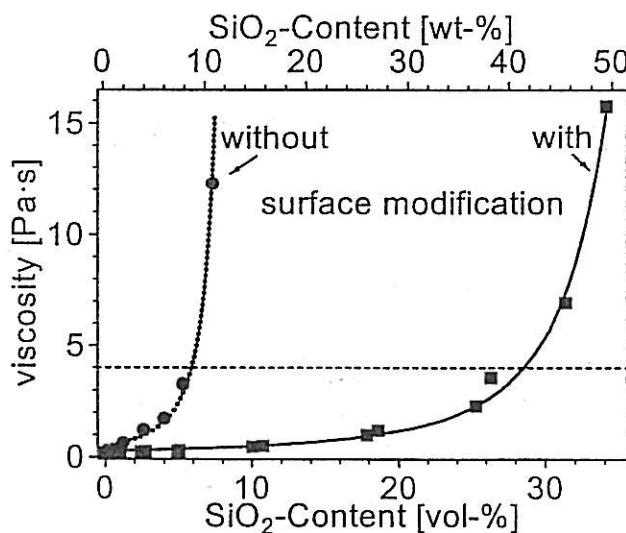


FIGURE 3

Viscosity of GPTS based NANOMER adhesive depending on the content of nanosized silica without (left) and with (right) surface modification (dashed line = limit of application in fiber-chip-coupling)

FIGURE 3 clearly shows that for the incorporation of SiO<sub>2</sub> particles without surface modification a tremendous increase of viscosity is obtained for filler contents of a few percent only, which can be attributed to particle-particle and particle-matrix interactions. For the use of micro dispensers and for fiber-chip-coupling with narrow joint gap of only a few  $\mu\text{m}$  an upper viscosity limit of only 4 Pa·s is given [1]. Furthermore, it was shown that

the pot life of the filled adhesives could be increased from less than 1 week for a composite containing 2 vol-% of unmodified filler particles to more than 1 year for a content of about 20 vol-%, in case of the surface modified particles. The surface modification was carried out as reported in [5]. This can be explained by the prevention of particle-particle and particle-matrix interactions due to electro-sterical shielding of the  $\text{SiO}_2$  nanoparticles. The filled Nanomer adhesives exhibited excellent transparency in the UV-VIS range and dilatometer measurements showed that the cte could be decreased from about 75 ppm/K down to 30 ppm/K for a filler content of about 15 vol-% [12]. Shrinkage was determined to be about 1 %.

To investigate the curing behavior of the NANOMER adhesives, and to compare it to the commercial epoxy resin based adhesive, layers of about 1 cm in diameter and 1 mm in thickness of both materials, having a comparable refractive index, were UV cured for 180 seconds at 75 mW/cm<sup>2</sup>. The microhardness of the adhesives was investigated directly and 24 hours after the UV exposure. The results are presented in FIGURE 4.

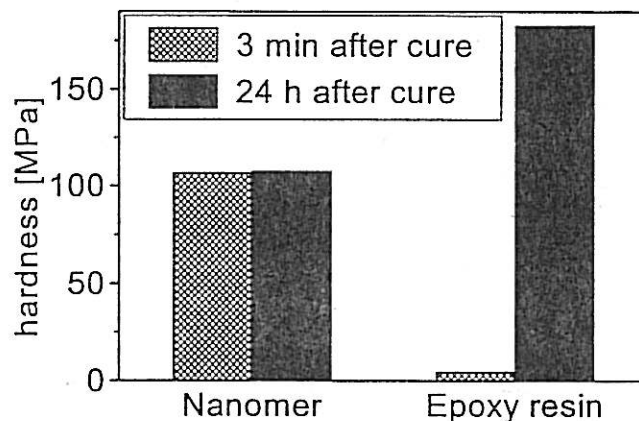


FIGURE 4

Micro hardness of a NANOMER based adhesive (left) and a epoxy resin based adhesive (right) directly and 24 h after curing

FIGURE 4 shows, that the NANOMER adhesive reaches its final hardness immediately after curing in contrast to the epoxy resin based adhesive, which was still liquid after the UV exposure and reached its final hardness after post curing for several hours. This may be explained by the presence of the Si-O-Si backbone with a high degree of condensation in the NANOMER adhesives, which is already formed in the liquid state and leads to the earlier obtention of the final hardness after polymerization of the epoxy groups. Furthermore, it could be assumed, that UV curing has a higher efficiency in the case of the

NANOMER. To investigate this hypothesis, DSC measurements of the cured adhesives of both types were carried out. The results are given in FIGURE 5.

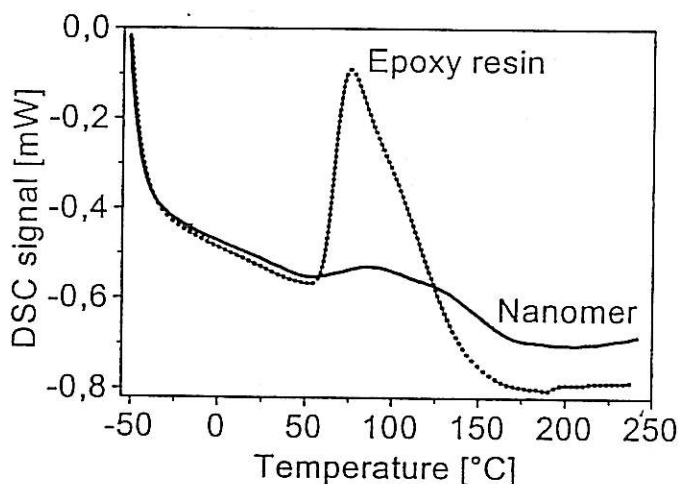


FIGURE 5

Comparison of the thermal post-curing of a NANOMER adhesive and the epoxy resin based adhesive by DSC measurements of the adhesives 24 hours after UV-curing

It could be shown, that the thermally initiated post-curing of the NANOMER adhesives was much less than in the case of epoxy resins (FIGURE 5). Again, a detailed discussion of this result is not possible, because the composition of the epoxy resin based adhesive is not known and therefore the chemical nature of the thermally activated post curing process cannot be discussed. Furthermore, the conversion rate of the epoxy groups of the Nanomer adhesives has not yet been investigated.

#### 4 CONCLUSION

It could be shown that UV curable inorganic-organic nanocomposites have an interesting potential for the use in the fabrication of optical components like fiber-chip-couplers. Their main advantage is the possibility to tailor their properties (refractive index, thermal expansion coefficient etc.) in a wide range in order to match to a given bonding problem. Disadvantages of epoxy resins or acrylate based adhesives, which are currently used to bond optical devices, could be effectively diminished. UV curing of the NANOMER adhesives is faster than UV curing of epoxy resin based adhesive, which provides the possibility to shorten production cycles and to reduce the high costs of fixation during the curing process.

## 5 ACKNOWLEDGMENTS

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