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UV-CURABLE EPOXY BASED NANOCOMPOSITE ADHESIVE FOR APPLICATIONS IN INTEGRATED OPTICS

Th. Koch, M. Mennig, H. Schmidt

Institut für Neue Materialien gem. GmbH, Im Stadtwald, D-66123 Saarbrücken

A UV-curable epoxy based adhesive was filled with nanosized SiO_2-particles with particle diameters of about 10 nm (SiO_2-content in the composite adhesives up to 35 wt.-%). Viscosities of the filled uncured adhesives were kept low at about 1000 mPa·s to 2000 mPa·s by surface modification of the particles. Volume shrinkage rate was reduced from 5.0 % (unfilled system) to 3.6 % in the case of a composite material with 20 wt.-% (approx. 12 vol.-%) nanosized SiO_2. Hence the coefficient of thermal expansion in a temperature range from -50 °C to 100 °C, was reduced from $70 \cdot 10^{-6}$ K^{-1} to $57 \cdot 10^{-6}$ K^{-1}. The refractive index decreased from 1.525 to 1.514 at a wavelength of 644 nm. Transmission electron microscopy (TEM) investigations demonstrate that the nanosized SiO_2-particles are not agglomerated in the cured material.

1 INTRODUCTION

State of the art in assembling components for integrated optical devices (e.g. fibre-chip coupling) is bonding with UV-curable acrylic or epoxy based adhesives[1,2]. These pure organic adhesives show several disadvantages, namely a high shrinkage rate during polymerisation and a high coefficient of thermal expansion (see FIGURE 1).

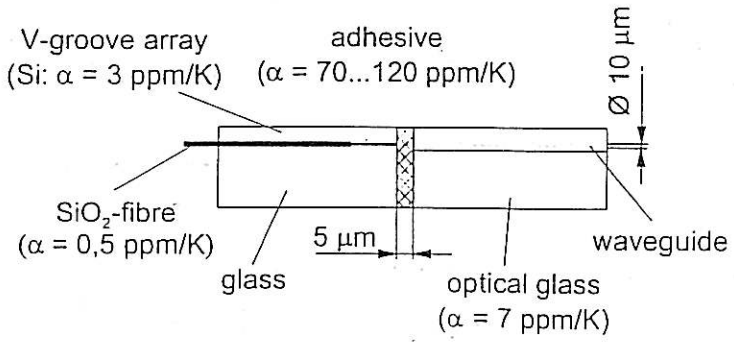

FIGURE 1
Assembly in fibre chip coupling

FIGURE 1 shows an assembly for fibre chip coupling, consisting of a planar waveguide component (optical glass) and a V-groove array (silicon) for several optical fibres (SiO_2). The adhesive layer with a thickness of 5 µm lies in the path of the ray of light with a diameter of about 10 µm.

Shrinkage during the curing process can cause an irreversible misalignment of the adherends. Reversible misalignment occurs on changes in temperature caused by strong mismatch of the coefficients of thermal expansion. These misalignments result in coupling losses in the very precisely aligned (± 0.1 µm) joints.

It is well known that inorganic filler particles incorporated in an organic adhesive matrix are able to minimise shrinkage and decrease the coefficient of thermal expansion in the composite material[3,4]. In this field of application the composite adhesive has to fulfil some special requirements. It lies within the ray of light and so the adhesive has to be transparent to wavelength of light used in fibre optics (800, 1300, 1550 nm). The viscosity of the uncured adhesive has to be lower than 4000 mPa·s in order to allow the adhesive to enter the small gap of 5 µm between the adherends by capillary forces.

The filler particles must not lead to optical loss caused by reflection and scattering. In order to reduce optical loss caused by reflection, the refractive index of the adhesive should be minimised.

The scattering loss caused by small particles in a homogeneous matrix can be described using the formula for Rayleigh scattering in the first approximation[5], which leads to EQUATION 1.

$$\gamma \approx \left[R^3 \cdot \frac{1}{\lambda^4} \cdot c_v \cdot \left(\frac{n_p^{\,2} - n_0^{\,2}}{n_p^{\,2} + 2n_0^{\,2}} \right)^2 \right] \qquad \text{EQUATION 1}$$

γ : optical loss
R : radius of the particles
λ : wavelength
c_V : volume fraction of the particles
n_P : refractive index of the particles
n_0 : refractive index of the matrix

The scattering loss is proportional to the particle radius to the power of 3. For a given wavelength and refractive indices of matrix and filler particles, extremely small particles have to be used in order to minimise the scattering loss.

Therefore, the aim of this paper was to develop a method for the incorporation of nanosized SiO_2 particles into an organic adhesive matrix in order to minimise shrinkage during curing and the coefficient of thermal expansion (cte) without notable scattering losses.

2 EXPERIMENTAL

2.1 SYNTHESIS OF ADHESIVES

A UV-curable epoxy based adhesive (Vitralit®) provided by Panacol-Elosol GmbH (Oberursel, Germany) was used as a matrix material. Nanosized SiO_2-particles were incorporated with different contents up to 35 wt.-% (23 vol.-%) using a colloidal silica sol in isopropanol (IPA-ST®, Nissan Chemicals). In an initial step a quaternary ammonia salt (tetrahexylammonium hydroxide) was added to the colloidal silica sol, which was then mixed with the adhesive by stirring for 5 minutes at room temperature. Finally the isopropanol was removed by distillation. A detailed description is given in DE 195 12 427[6].

2.2 CHARACTERIZATION OF ADHESIVES

The adhesives were cured using a high-pressure mercury UV-lamp (UVP-200, Panacol-Elosol GmbH), for 180 seconds with an intensity of 75 mW/cm^2 (measured with UVM-100, Panacol-Elosol GmbH).

Shrinkage was determined by comparing the density of the adhesive in the uncured state (pycnometer) and cured state (Archimedes buoyancy method). Coefficients of thermal expansion were measured with a Mettler Toledo TMA 40 dilatometer (sample thickness 1 mm). To characterise bond strength, pressure shear experiments were carried out (float glass samples 20 x 20 mm, 5 mm intersection) using a Zwick 1446 universal testing machine. Refractive indices were measured with a Pulfrich PR 2 refractometer (Zeiss, Jena). Samples of cured adhesive were ultramicrotomed in a Reichert ultracut. The slices obtained, with a thickness of approximately 150 nm, were investigated in a transmission electron microscope (Jeol JEM 200 CX).

3 RESULTS

By the preparation route described above, it was possible to prepare completely transparent bulk samples of the adhesive by UV-curing for filler contents of up to 35 wt.-% (23 vol.-%) SiO_2.

FIGURE 2 shows photographs of a drop of unfilled adhesive (left) and a drop of filled adhesive (12 vol.-%, right) after UV curing. The thickness of the samples is approximately 1.5 mm. The shrinkage of the unfilled adhesive was determined to about 5.0 vol.-%, leading to a structured surface after curing. For the filled sample a shrinkage of only 3.6 vol.-% was obtained and the surface of the adhesive drop remained smooth after UV curving. The relative reduction in shrinkage (28 %) is higher than the filler content (12 vol.-%), which might be due to interfacial effects of the composite material. On the other hand, it is astonishing that the reduction in shrinkage from 5 % down to 3.6 % could completely prevent the formation of structured surface. It may be assumed that the homogenity of the curing process is increased by the filler, but further investigations will be necessary to explain this phenomenon.

FIGURE 3 shows a transmission electron microscope picture of a slice ultramicrotomed from cured nanocomposite adhesive (12 vol.-% SiO_2) with a thickness of approximately 150 nm.

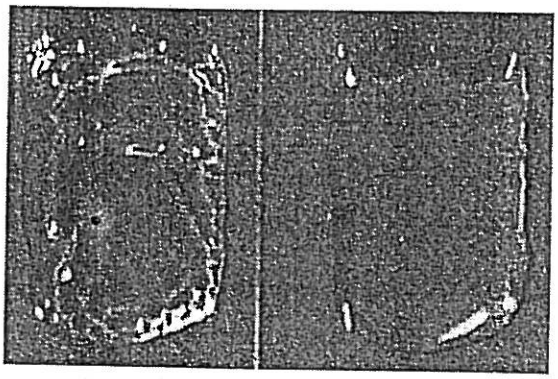

FIGURE 2
Picture of unfilled (left) and filled (right; 12 vol.-%) adhesive; thickness of the cured drops approx. 1.5 mm

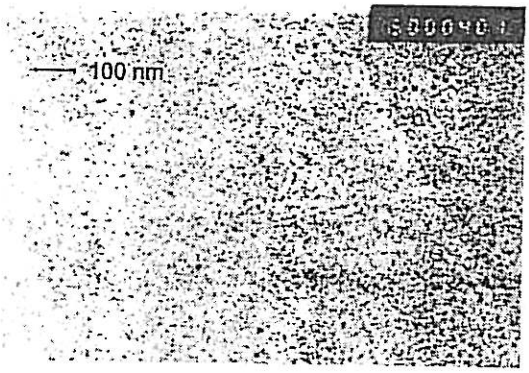

FIGURE 3
TEM image of an adhesive with 12 vol.-% SiO_2 (sample approx. 150 nm thick)

The TEM image shows well dispersed SiO_2 nanoparticles with an average diameters of about 10 nm.

Due to the excellent transparency it was possible to determine the refractive index of the filled adhesive. The result is shown in FIGURE 4.

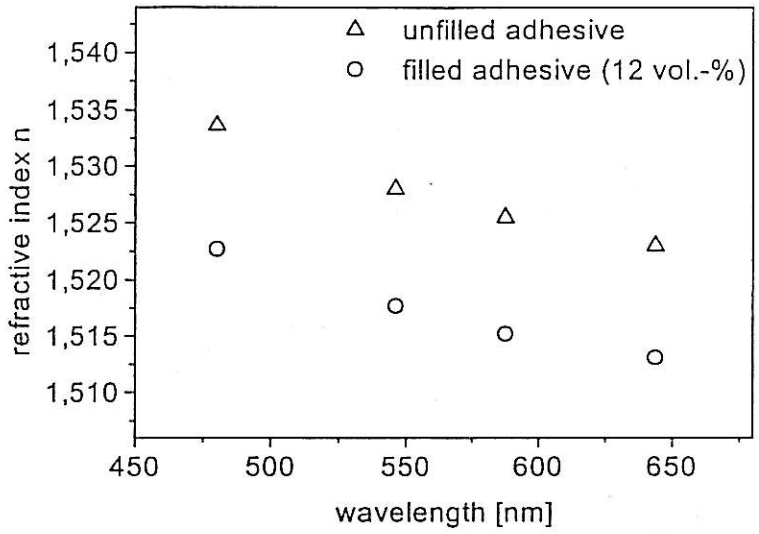

FIGURE 4
Refractive index as function of wavelength for unfilled and filled adhesive (12 vol.-%) after UV-curing

FIGURE 4 clearly shows that the refractive index decreases from 1.525 ± 0.001 (unfilled; 644 nm) to 1.514 (filled, 12 vol.-%). The refractive index of the filler particles was determined by the index matching method[7] to be 1.457 ± 0,005 for this wavelength. The calculation of the refractive index of the composite, with these data, leads to a value of 1.517 ± 0,002, which is within the error of measurement of the experimental result.

As one can see from FIGURE 4, the dispersion of the adhesive remains unchanged by the filler particles. Therefore it may be assumed that a comparable decrease of the refractive index by the filler will also be obtained for the NIR. This is important for tele-communication application because coupling losses by Fresnel reflection can be reduced this way.

Thermomechanical analysis was performed in order to determine the influence of the filler on the coefficient of thermal expansion (cte) of the composite adhesive. FIGURE 5

shows the thermal expansion of unfilled and filled adhesive bulk samples (1 mm in thickness) after UV curing. In order to exclude effects caused by thermal postcuring[8] only the second measurement run was used.

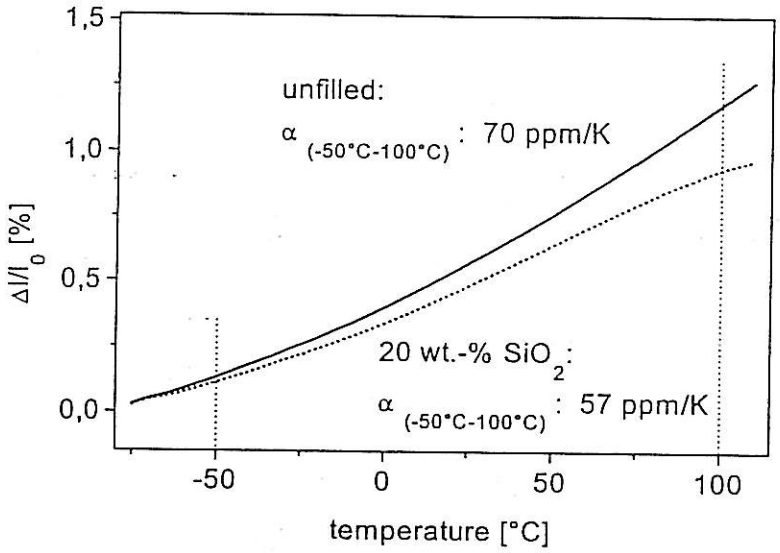

FIGURE 5
Thermal expansion of pure matrix compared with composite (20 wt.-% SiO_2)

FIGURE 5 shows that in the temperature range between -50 °C and 100 °C (which covers the telecommunication standards) the cte ot the unfilled adhesive was reduced from 70 ppm/K down to 57 ppm/K by filling the matrix with 20 wt.-% (appr. 12 vol.-%) nanosized SiO_2. This reduction (19%) is higher than the volume concentration of the particles. Again it has to be assumed that this is due to interfacial effects of the composite. From FIGURE 3 it was evident that the nanosized filler particles are not agglomerated. With the particle size of about 10 nm one can estimate the total surface area of the SiO_2 nano particles to be about 72 m^2 per cm^3 volume of composite materials. With respect to this large value it seems plausible to assume that interfacial effects can change macroscopic materials properties if the structure of the matrix materials is modified in the interfacial region.

After showing that the optical properties, the shrinkage and the cte could be improved by the nanosized SiO_2 filler, it was necessary to investigate the influence of the filler particles on the bond strength of the adhesive. It could be shown that the pressure shear strength of single lap float glass samples was reduced from more than 30 N/mm^2 (adhesive without filler) to 15 N/mm^2 (12 vol.-% SiO_2). In both cases adhesion failure occurred. It is assumed that the strong decrease in bond strength is due to wetting of the filled adhesive on the glass surface, since the viscosity of the uncured adhesive was increased from 400 mPa·s to about 1200 mPa·s for the filled product. Another reason could be the „shielding" of Si-OH groups of the glass surface by the cation of the ternary ammonium salt which was used for the surface modification of the SiO_2 nanoparticles. This surface modification is necessary to obtain high filler contents without increasing the viscosity of the uncured adhesive in an unacceptable way[9]. On the other hand a bond strength of 15 N/mm^2 is sufficient for telecommunication applications (limit 10 N/mm^2 [10])

4 CONCLUSION

The investigations have shown that nanocomposite adhesives combine the advantages of high transparency and tailoring of refractive index with the advantages of inorganic fillers for reduced shrinkage and lower coefficient of thermal expansion. Therefore, these adhesives are very interesting for optical applications.

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