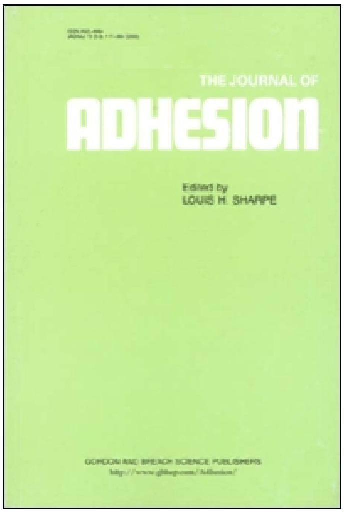

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UV-Curable Transparent Adhesives for Fabricating Precision Optical Components*

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UV-curable transparent epoxy adhesives have been specifically developed for the fabrication of optical communictions precision devices. The newly developed adhesives using cylohexane type fluoro-epoxy as the base resin and speherical quartz filler have extremely low volume shrinkage of 1.2% during curing and the cured adhesives have low thermal expansion coefficient of less than $2 \times 10^{-5}/°C$. Sheets of the adhesives are colorless and transparent to visible light because the refractive index of the epoxy matrix resin is matched to that of the quatz filler. These highly transparent adhesives can be cured to a depth of more than 5 mm by using 10 mW/cm^2 UV-irradiation for 30 min. They also have high adhesive strength and good durability. Therefore, they can be used in the fabrication of optical components that require submicron positioning accuracy.

KEY WORDS: Cyclohexane-type fluoro-epoxy adhesives; optical communications devices; sub-micron positioning accuracy; speherical quartz filler; low curing shrinkage; low thermal expansion coefficient; depth of cure; high strength; durability.

1. INTRODUCTION

UV-curable adhesives which set rapidly where widely used in the fabrication of optical and electrical components because they offer good device productivity. Optical components require precise bonding with sub-micron positioning accuracy because these devices have tight positioning tolerances. Since UV-curable adhesives take only a few minutes to cure at room temperature, it is easy to align optical components while assembling them. In contrast, thermosetting adhesives currently in use take 3–6 hours to cure completely at high temperatures of 60–100°C. There are, however, only a few conventional UV-curable adhesives, and they cannot be used for high-precision optical components because they-shrink more than 3% during curing and have a high thermal expension coefficient of more than $4 \times 10^{-5}/°C$, as shown in Figure 1.

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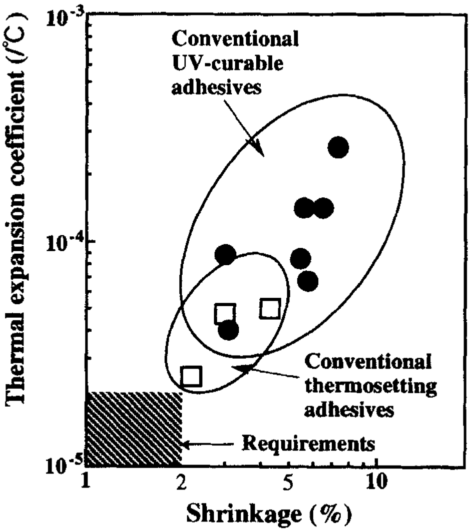


FIGURE 1 Thermal expansion coefficient and shrinkage during curing of epoxy adhesives.

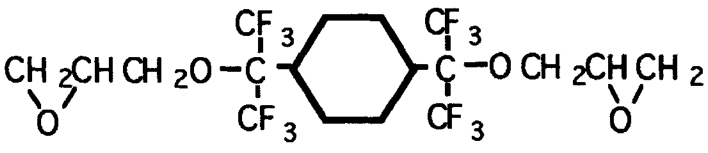
We have previously investigated the UV-curability of filler-containing adhesives that have low shrinkage and low thermal expansion coefficient[1]. We have recently developed highly transparent UV-curable adhesives that have higher precision and depth of cure than previous ones.

This paper describes the properties of these transparent precision adhesives including their reactivity and durability for optical-component use. Application to laser diode modules is also presented.

2. EXPERIMENTAL

2.1. Materials

Cyclohexane type fluoro-epoxy (diglycidylether of bis-(1, 1, 1, 3, 3, 3 hexafluoropropyl) cyclohexane) as shown below was used as a base resin[2] to control the refractive index of the epoxymatrix.



As shown in Table I, Bisphenol type epoxy resins (Epikote 828, Yuka-Shell Epoxy Co., Tokyo), alicyclic epoxy diluent (vinyl cyclohexene dioxide), silanecoupling agent (γ-glycidoxypropyltrimethoxysilane), and quartz filler (Tatsumori Ltd., Tokyo) were added. Then we used the onium salt (triarylsulfonium-SbF_6 salt) as a cationic

TABLE I
Formulation of UV-curable transparent adhesives

Ingredients	Composition (parts by weight)
Base resins[1]	100
Diluents[2]	10–30
Filler[3]	0–200
Silane coupling agent[4]	2–5
Photoinitiator[5]	2–5

[1] Cyclohexane type fluoro-epoxy (Reference 2) and bisphenol type epoxy
[2] Alicyclic epoxy and fluoro-epoxy
[3] Quartz powder
[4] Epoxy silane
[5] Onium salt

polymerization initiator. Quartz fillers such as spherical synthesized quartz powder, high-purity split quartz powder, fused quartz powder and crystalline quartz powder were used as shown in Table II.

2.2. Test Procedure

Curing shrinkage was calculated from the specific gravities of the adhesives, which were measured before and after curing. The ones before curing were measured with a digital density meter DMA48 (Anton Paar Co., Austria). Those of the cured adhesives were measured by the water substitution method.

Thermal expansion coefficients were measured with a thermal mechanical analyzer. Refractive indices were measured with an Abbé refractometer at 25°C. Transmittance spectra were measured for 1 mm casting sheet samples using a Hitachi U-3000 spectrometer. Sheet samples were constructed from a 1-mm-thick Teflon spacer and an FEP-Teflon mold-releasing film, placed between two plates of quartz glass and cured using UV-irradiation. Curing was done using a UV light source (400-W metallic halide-vapor lamp, Phillips HPA-400W) at a distance of 40 cm. UV-curing was carried out at a UV-irradiation dose of approximately 10 mW/cm^2.

The depth of cure was measured using a mold-holder as shown in Figure 2. The mold-holder filled with UV-curable adhesive resin was covered by an FEP-Teflon

TABLE II
Fillers and transmittance of adhesives with quartz filler

Adhesives[1]	Filler (Shape)	Diameter(μm)	Content(phr)	Transmittance[2](%)
A	Synthesized quartz[3](Sphere)	0.5–4.5	120	90
B	Synthesized quartz(Splinter)	6–50	120	18
C	Fused quartz(Splinter)	0.2–7	92	19
D	Crystalline quartz(Splinter)	0.2–2	109	1

[1] Cured adhesive resins have a refractive index of 1.46, the same as quartz
[2] 1-mm-thick sheets at 1.3 μm
[3] Surface-treated powder

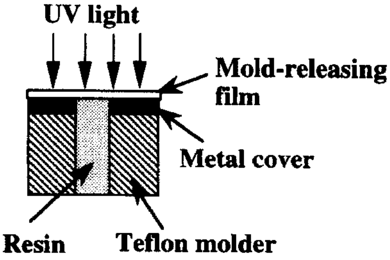


FIGURE 2 Method of measuring depth of cure.

mold-releasing transparent film on top, and the resin was irradiated by UV-light through the strip of film for a specific time. The uncured part of the adhesive resin that was removed from the mold-holder after UV-exposure was wiped with a fresh gauze. The height of the cylinder of cured resin was measured with a micrometer.

Curing speed was evaluated from the change in torsional shear adhesive strength *versus* the UV irradiation time using the test specimen shown in Figure 3(a). The adhesive materials were joined between a quartz glass plate and an aluminum rod ($5 \times 5 \times 20$ mm), and UV light was irradiated through the quartz glass.

The tensile shear adhesive strength was measured by placing quartz-glass single overlap joints [Fig. 3(b)] in a sample holder and using an Instron testing machine at a crosshead speed of 5 mm/min. at 25°C.

The water resistance was assessed by subjecting the joints shown in Figure 3(b) to wet heat treatment for various times, and then measuring the adhesive strength at 25°C. The water resistance was also assessed by observing bubble formation and peeling on the adhesive interface caused by wet heat treatment on cladding glass plates as shown in Figure 4.

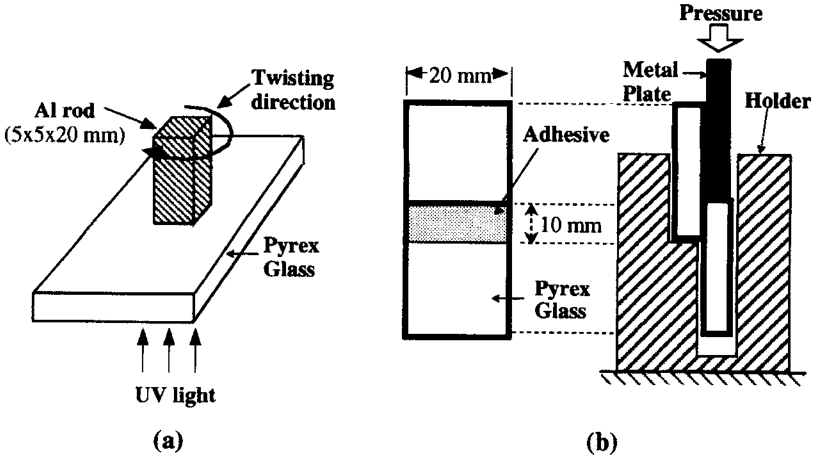


FIGURE 3 Testing methods of (a) torsional shear adhesive strength and (b) tensile shear adhesive strength.

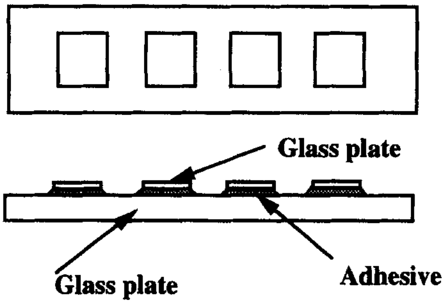


FIGURE 4 Bonding layer defect test specimen for wet heat treatment.

The surfaces of the cured epoxy adhesives containing quartz filler were fractured in liquid nitrogen and examined to determine the wettability between matrix resin and filler particles using a scanning electron microscope (SEM) operated at 5 kV. SEM specimens were coated with a thin Pt film (10Å) by sputtering.

3. RESULTS AND DISCUSSIONS

(1) UV-Curability

Figure 5 shows the effect of UV irradiation on the torisional shear adhesive strength of two adhesive formulations as a function of time. Adding 150 phr (parts by weight per hundred parts of resin) of a quartz powder hardly affected the curing speed of the fluoro-epoxy adhesive compounds. However, the conventional epoxy

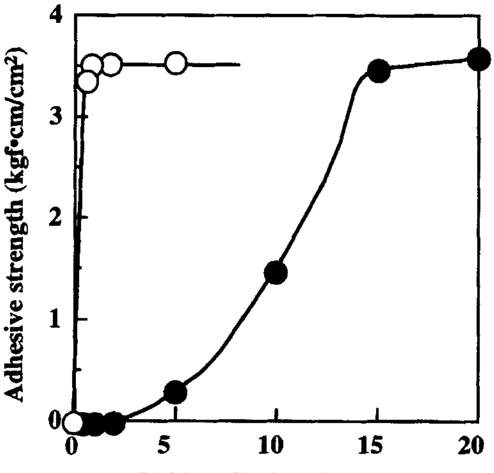


FIGURE 5 Dependence of torsional shear adhesive strength at 25°C on UV irradiation time; (○) Transparent UV-curable precision adhesive; (●) Conventional non-transparent UV-curable precision adhesive.

adhesive compound containing 120 phr of a ceramic powder had a slow curing speed of more than 10 min. These results indicate that fluoro-epoxy adhesives containing a quartz filler can be cured by UV-irradiation within a few minutes because the UV-curable fluoro-epoxy adhesive compounds have good transmittance in the UV wavelength range of less than 0.4 mm, as shown in Figure 9.

Since the UV-curable fluoro-epoxy adhesives containing quartz powder are capable of fast adhesion and fixation within a few minutes at room temperature with UV irradiation, it is easy to fix optical components with sub-micron accuracy when assembling them.

(2) Curing Shrinkage and Thermal Expansion Coeffient

Figure 6 shows the effect of the quartz-filler content on curing shrinkage and thermal expansion coefficient. Both properties decrease with increasing filler content, and reach a shrinkage of 1.2% and an expansion of $2 \times 10^{-5}/°C$ at a filler content of 120 phr. The thermal expansion coefficient decreases with increasing filler content, and reaches $1.7 \times 10^{-5}/°C$ at 175 phr. The mechanical strength of the adhesive was poor and its viscosity increased rapidly above 175 phr, because filler particles are close to each other as the filler content increases and the interaction between filler particles becomes stronger, the fluidity of the adhesive resin decreases, and the elongation and toughness of the cured resins also decrease. The results show that the optimum amount of filler is 100–150 phr.

(3) Transparency

Figure 7 shows the relationship between the transmittance of the adhesive sheets and the refractive index of the matrix resins after curing. As the refractive index of

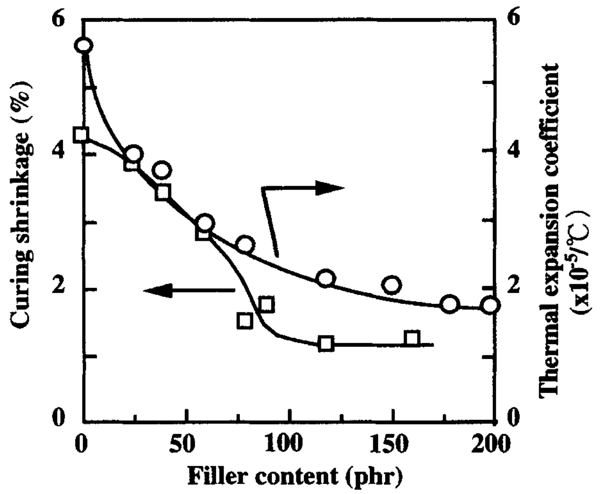


FIGURE 6 Dependence of shrinkage during curing and thermal expansion coefficient on filler content of adhesives.

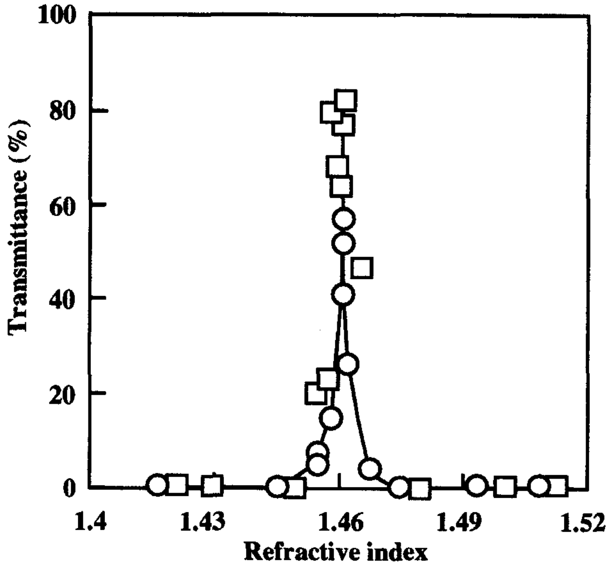
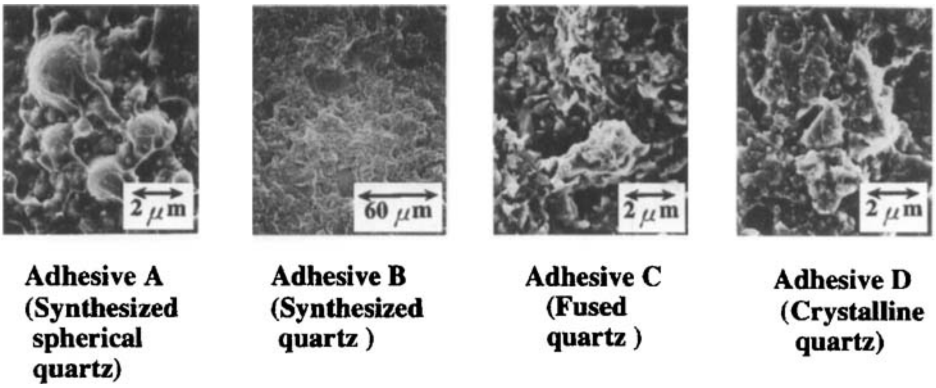


FIGURE 7 Dependence of transmittance at 0.589 μm (○) and 0.4 μm (□) of adhesive sheets on refractive index (n_D) of matrix resins.

the matrix resins approached that of the quartz filler ($n_D = 1.46$), the transmittance of the sheets increased. The light was scattered by the mismatch of refractive indices among the matrix resin, the filler, and the air layer. To achieve high transparency, we used fluoro-expoxy resin to match the refractive index of the matrix resin to that of the spherical quartz filler. The filler was given good wettability by the matrix resin, as shown in the SEM image (Fig. 8), by treating the surface with a suitable silane coupling agent. Other quartz fillers have poor wettability by the matrix resin, as shown in Figure 8. Therefore, the transmittance of the adhesive sheets is low as



Adhesive A (Synthesized spherical quartz)

Adhesive B (Synthesized quartz)

Adhesive C (Fused quartz)

Adhesive D (Crystalline quartz)

FIGURE 8 SEM images of fractured surface for cured resins filled with various quartz powders (fractured in liquid nitrogen).

shown in Table II, even though the refractive index of their quartz filler was also matched to that of the matrix resin.

Cured sheets of the adhesive with a filler content of 120 phr are colorles and transparent to visible light. Uncured adhesive compounds are white, non-transparent pastes. The refractive index of the matrix resin is slightly smaller than that of quartz filler, because the refractive index of the resin increases by about 0.01 through curing.

As Figure 9 shows, the transmittance through a 1-mm-thick sheet of the new transparent precision adhesive was about 80–90% in the wavelength range from 0.6 to 1.6 μm and decreased for wavelengths below 0.6 μm, reaching zero at about 0.3 μm. Moreover, at wavelengths of 1.2 μm and 1.4 μm, absorption attributable to C—H and O—H oscillation, was observed.

(4) Depth of Cure

Figure 10 shows the effect of the quartz-filler content on depth of cure for various UV-irradiation times at a UV-irradiation dose of approximately 10 mW/cm^2. Depth of cure decreased with increasing filler content, and became constant at a filler content of 50 phr. Since the UV-light scattering due to the mismatch of refractive indices among the matrix resin, the filler, and the air layer increased with increasing filler content, the depth of UV-light penetration into the adhesive layer decreased. However, the UV-light transmittance of the adhesive layer increased wtih increasing filler content, because the quartz filler is very transparent to UV-light. Therefore, the depth of cure became constant according to the sum of these effects as shown in Figure 10.

Figure 11 shows the cure depth of transparent and non-transparent adhesives *versus* UV-irradiation time. The transparent fluro-epoxy adhesive containing

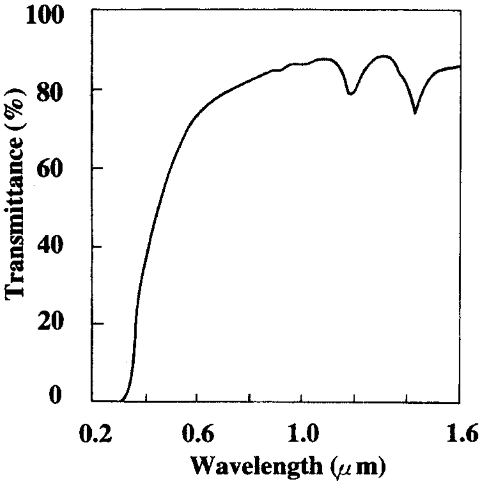


FIGURE 9 Transmittance spectra of a 1-mm-thick sheet of new transparent precision adhesive.

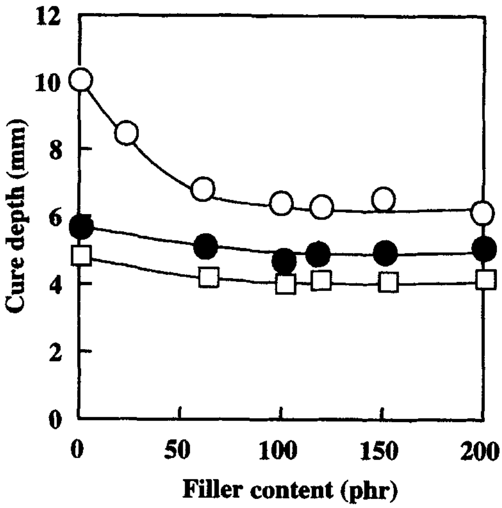


FIGURE 10 Effect of the quartz-filler content on the depth of cure (□) UV irradiation time for 20 min, (●) for 30 min, (○) for 60 min.

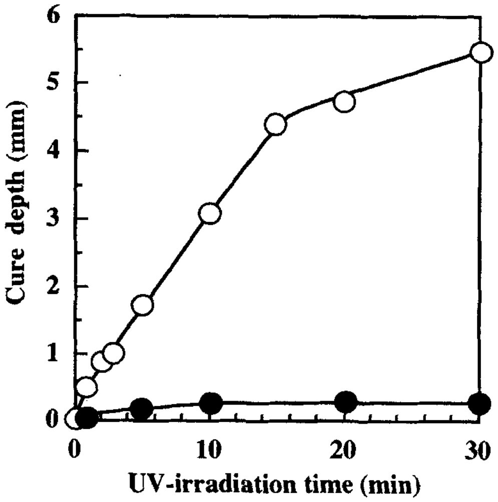


FIGURE 11 Cure depth of adhesives against UV-irradiation time ○ Transparent type; ● Non-transparent type.

120 phr of spherical quartz filler was cured to a depth of more than 5 mm by 10 mW/cm^2 UV-irradiation for 30 min. In contrast, the non-transparent bisphenol type epoxy adhesive containing 120 phr of ceramic filler could be cured to only 0.3 mm under the same conditions.

4. MAIN PROPERTIES OF THE NEW ADHESIVES AND THEIR APPLICATION TO OPTICAL COMPONENTS

4.1. Main Properties

The properties of the new precision adhesives are compared in Table III with those of conventional UV-curable and thermosetting adhesive systems. The new adhesives have many superior properties. The extremely low volume shrinkage of 1.2% during curing is the lowest shrinkage among the adhesives.Moreover, it is lower than that of any previously developed UV-curable non-transparent precision adhesives[1].

The cured adhesives have low thermal expansion coefficient of less than $2 \times 10^{-5}/°C$. Sheets of the adhesives are colorless and transparent to visible light.

Two adhesives have sufficient initial adhesive strength of more than 18 MPa: our new UV-curable epoxy adhesives and conventional heat-curable adhesives. However, the adhesion of the conventional epoxy adhesive system markedly deteriorates to less than 1/5 after exposure to 85% RH at 85 °C for 14 days. The adhesive strength of the conventional UV-curable acrylate adhesive is less than 4 MPa. The new UV-curable adhesive compounds, which contain a suitable silane coupling agent[2], are more water resistant because their adhesive strengths are greater than the fracture strength of Pyrex glass, even after 24-hour immersion in boiling water. Moreover, the adhesion strength of the new UV-curable adhesives was maintained after exposure to 85% RH at 85°C, for 1000 hours, and there were no signs of peeling or bubbling on the adhesive surface, as shown in Figure 4. The new adhesives have high adhesive strength and good durability.

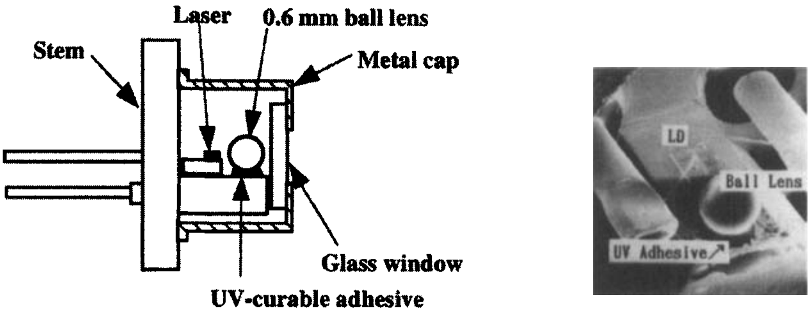
4.2. Application to the Fabrication of Optical Devices[3]

The new precision adhesives were successfully applied to the fabricationof a laser-diode module (LDM) and an optical modulator. Figure 12(a) shows a cross-section of the laser package. A 0.6 mm-diameter micro-ball lens was fixed near the laser using the precision adhesive, as shown in the SEM image [Fig. 12(a)]. For this LDM, the lens bonding accuracy must be within 1 μm. The lens movement during

TABLE III
Main properties of precision adhesives

Property	New	Conventional	
	(UV-curable)	(UV-curable)	(Thermosetting)
Curing time	1–5 min (Room temp.)	< 1 min (Room temp.)	2 h (70 °C)
Shrinkage during curing (%)	1.2	3	2
Themal expansion coefficient ($\times 10^{-5}/°C$)	2	4	3
Tensile shear strength (MPa) Dry	> 19.6	3.7	18.6
Tensile shear strength (MPa) Wet[1]	15.7	2.2	3.7

[1]After exposure to 85% RH at 85 °C for 14 days



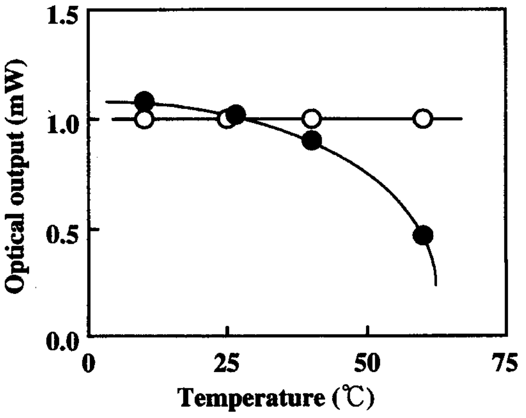
(a) Laser collimator module

(b) SEM image

GURE 12 (a) Cross-section of the laser module with a micro-ball lens fixed by the UV-curable hesive. (b) SEM image of the micro-ball lens in the module.

V-curing was reduced to sub-micrometer order because the shrinkage was only 2%. This bonding accuracy is easily achieved by a 1-μm pre-offset to cancel the ovement during the curing. Other adhesives cannot be used because of their high rinkage.

Figure 13 shows the temperature characteristics of the LDM operated under APC nditions (Auto Power Control: the fiber output power is controlled by keeping the onitor photo diode current constant at all temperatures). Since the module fixed ith conventional adhesive having a large thermal expansion coefficient 0 × 10^{-5}/°C) shows a large error in APC operation, the fiber output light power lls drastically at higher temperatures. This result strongly indicates that the disacement of the ball-lens caused by the expansion of the adhesive is too large to mpensate for by adjusting the current. In contrast, the module fixed with the new



GURE 13 Temperature characteristics of APC-operated LD modules fabricated with new precision hesive (○) with thermal expansion coefficient $\alpha = 2 \times 10^{-5}$/°C and conventional adhesive (●) with =30 × 10^{-5}/°C.

adhesive shows good APC operation in the temperature range 10–60°C because the resin expands less.

5. CONCLUSIONS

UV-curable transparent expoxy adhesives having extremely low volume shrinkage of 1.2% during curing and low heat expansion coefficient of less than $2 \times 10^{-5}/°C$ were developed using cyclohexane type fluoro-epoxy as the base resin and spherical quartz filler surface treated with a suitable silane coupling agent. These adhesives are readily applicable as precision adhesives for the fabrication of optical components, which require submicrometer positioning accuracy, since they have low volume shrinkage, low thermal expansion coefficient, high depth of cure, high adhesive strength, and good durability. These qualities are advantageous for achieving low-cost optical components with excellent properties.

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