Fluorine-Containing Optical Adhesives for Optical Communications Systems

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SYNOPSIS

Fluroinated epoxy resin adhesives containing diglycidylether of bisphenol AF (DGEBAF) with a fluorine content of 25.7 wt % are developed for fabrication of optical communications devices. These adhesives, formulated with a diluent of butanediol diglycidylether (BDDG) and a curing agent of polyether polyamine (Q694), can be cured at a curing temperature as low as 65°C and exhibit high transparency of more than 80% in the wavelength range of 0.5–1.3 μm. Moreover, they significantly reduce return loss at optical-glass/adhesive interfaces because of the low refractive indices of ca. 1.52 and also improve heat durability of optical devices. They are successfully applied to submarine optical fiber transmission system.

INTRODUCTION

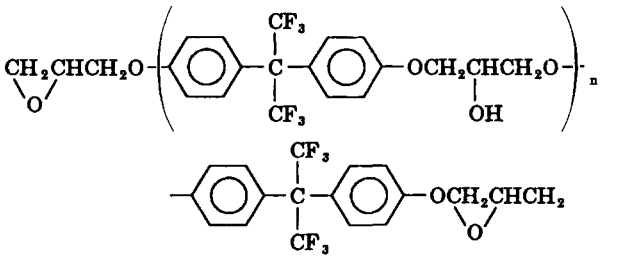
An optically transparent adhesive is a key material in fabrication of optical communications devices such as laser diode (LD) modules, avalanche photo diode (APD) modules, optical couplers, and optical dividers.[1,2] Epoxy resin have been widely used as optical adhesives because of their high transparency and high adhesive strength. Refractive indices (n_D^{20} = 1.54–1.57) of conventional epoxy resin adhesives, however, are relatively high compared to those of optical glasses in optical communications devices such as optical fiber (n_D^{20} = 1.46) and BK7 glass (n_D^{20} = 1.514). The resulting refractive index mismatching at adhesive joints induces considerable light reflection, which makes LD operation unstable. Low-temperature and rapid curability is also needed for optical adhesives, to prevent degradation of optical devices and fiber coating materials in the device fabrication process. Low viscosity and long pot life are also required for good workability. New specific optical adhesives, therefore, are required, especially for development of high performance optical communications systems.

Well-known methods for lowering the refractive index of organic materials are to introduce atoms and/or substituents having small polarization and large molecular volume into them. We have already reported that fluorination is effective in lowering the refractive index of polymers.[3–5] This work describes fluorine substitution in epoxy resins for improving their optical properties. The fluorinated epoxy resin compositions are formulated with a diluent and a curing agent for applying optical adhesive materials. The properties of fluorinated epoxy resin adhesives, such as refractive index, thermal stability, and adhesive strength, are affected by the degree of fluorination.

EXPERIMENTAL

Materials

2,2-Bis(4-glycidylphenyl ether) hexafluoropropane [diglycidylether of bisphenol AF (DGEBAF), I],



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which is synthesized from hexafluoroacetone, phenol, and epichlorohydrine according to a similar method described by Dammont, Sharpe and Schornhorn,[6] was used as a fluorinated epoxy resin. Synthesized DGEBAF is yellowish liquid with a viscosity at 25°C (η^{25}) of more than 200,000 cps. The epoxy equivalent weight (EEW) measured by the HCl–pyridine method was 275 and the refractive index at 20°C (n_D^{20}) was 1.518. Gel permeation chromatography (GPC) measurement clearly showed that the molar ratio of $n = 0/n = 1/n = 2$ in (I) was 85/12/3. The calculated value of fluorine atom content derived from the GPC result was 25.7 wt %.

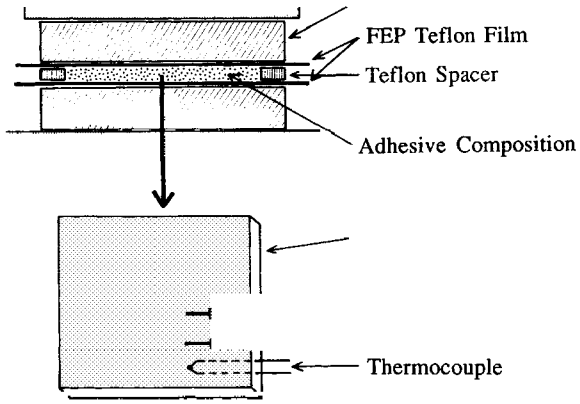
Diglycidyl ether of bisphenol A (DGEBA) (Epikote 828, Yuka Shell Epoxy Kabushiki Kaisha), a hydrocarbon analog of DGEBAF, was used as a nonfluorinated epoxy resin. The properties of the DGEBA system were compared with those of the DGEBAF system to investigate the effect of the fluorine containing substituent. The value of EEW was 189 and that of n_D^{20} was 1.574. Butanediol diglycidyl ether (BDDG, Aldlich Chemical Co.) was used as a low viscosity diluent. The value of n_D^{20} was 1.461, EEW was 101, and η^{25} was 25 cps. An aliphatic polyether polyamine (EPOMIC Q694, Mitsui Petrochem. Ind. Epoxy Corp.) was used as the curing agent. Values of active hydrogen equivalent weight was 80, n_D^{20} was 1.461 and η^{25} was 76 cps.

A conventional optical adhesive, C-OA was used as a comparison. Epoxy resin of C-OA is a mixture of DGEBA and diglycidyl ether of polyglycol, and its curing agent is a mixture of modified aliphatic polyamine and modified heterocyclic polyamine. The C-OA was cured for 8 h at 60°C.

Before sample preparation, foams in the stirred mixture of the epoxy resin and the curing agent were entirely removed in a vacuum oven for 5 min to prevent appearance of voids in cured adhesives. Defoaming temperature was 25–40°C and pressure was about 1 mm Hg.

Epoxy resin adhesive systems usually show exothermisity during cure, and the properties of cured adhesives vary with the magnitude of the exothermic heat. Cupples et al. reported that the influence of exothermic heat was negligible in a curing mass of less than 10 g.[7] Samples with a cured mass value of less than 10 g were therefore prepared.

Sheet samples of 100 × 70 × 1 mm with a thermocouple and optical fibers (50 GI) were prepared as illustrated in Figure 1. As expected, the effects of exothermic heat were able to be disregarded because



the measured temperature deviations during cure were within 1°C of the curing temperature in all adhesive systems. The sheet was cut into 10 × 10 mm pieces for refractive index measurement, and 25 × 10 mm for elastic moduli and light transmission loss measurements.

An ASTM D 1882 L-type dumbbell with 0.3 mm thickness, for tensile strength measurements, was prepared by a casting method. Copper and aluminum single lap joints, for tensile shear adhesive strength tests, were made in accordance with JIS K 6850. The adhesive layer thickness of the sample was less than 30 μm.

Three kinds of samples were prepared to investigate the properties of adhered parts in optical devices. Fiber end samples [Fig. 2(a)] which had been applied to LD modules and optical couplers were prepared for return loss measurements. Optical filter samples [Fig. 2(b)] and glass prism samples which had been used in optical couplers were also prepared for loss deviation measurements. The adhesive layer thicknesses of samples were less than 30 μm.

Refractive indices were measured at 20°C using Abbe's refractometer (Atago Co. Ltd.). Elastic moduli were measured at a frequency of 3.5 Hz and a temperature rising rate of 2°C/min using a dynamic viscoelastometer (Vibron DDV-III-EA, Orientech Corp.). Glass transition temperature (T_g) was evaluated to be a peak temperature of tan δ.[8,9] Tensile shear adhesive strengths and tensile strengths were measured at 1 mm/min crosshead speed and at 23°C by an Instron universal tester. Viscosities were measured at 25°C by a B-type viscometer (Tokyo Precision Instrument Co. Ltd.).

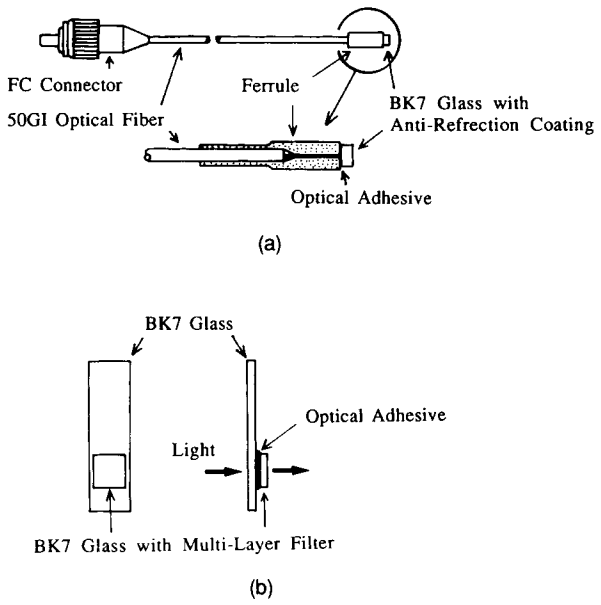


Figure 2 Structures of fiber end sample (a) and optical filter model sample (b).

Light transmission losses of cured resins and loss deviation of filter samples were measured with a spectrometer (Hitachi U-3400). Return losses were measured using an MR-91A (λ = 0.89 μm) and an MR-92A (λ = 1.30 μm) return loss tester (Anritsu). The loss deviation measurement system of prism samples is illustrated schematically in Figure 3.

RESULTS AND DISCUSSION

Fluorine Substitution Effects

Since optical adhesives were applied in light-transmission paths, optical transparency was the most important factor. DGEBA and its fluorinated DGEBAF system showed a sufficiently high transmittance value of more than 80% in the wavelength (λ) range of 0.5–1.3 μm (Fig. 4).

Figure 5(a) shows the DGEBAF content dependence of the refractive index at λ = 0.589 μm (n_D^{20}) in cured adhesives. The n_D^{20} value decreases linearly with increase in DGEBAF content, and reaches 1.521 in DGEBAF cured with Q694. This value is lower than that of a conventional optical adhesive (C-OA, 1.543). The n_D^{20} values of DGEBAF/DGEBA were insensitive to curing temperature. They did not change, within experimental errors of ±0.001, in the curing temperature range from 65 to 100°C.

Figure 5(b) shows reduction in n_D^{20} value with increasing fluorine content in cured resin. Here, Δn_D^{20} was calculated from

$$\Delta n_D^{20}(\%) = 100*(n_D^{20}{}_0 - n_D^{20}{}_F)/n_D^{20}{}_0 \quad (1)$$

where $n_D^{20}{}_0$ and $n_D^{20}{}_F$ are n_D^{20} values of the DGEBA system and the F g/cm^3 fluorine containing system, respectively. A refractive index (n) of an organic material is generally expressed by the Lorents–Lorens equation

$$(n^2 - 1)/(n^2 + 2) = [R]/(M/d) = [R]/V \quad (2)$$

where [R] is the molar refraction, M is the molecular weight, d is the density, and V is the molecular volume. The fluorine substituted system has relatively large [R] and V values because of the larger values of atomic refraction and covalent bond radius of the fluorine atom than those of a hydrogen atom (Table I). The increase in Δn_D^{20} (reduction in n_D) shown in Figure 5(b), which results from decrease in [R]/V, indicates that the fluorine substitution strongly effects an increase in V rather than [R].

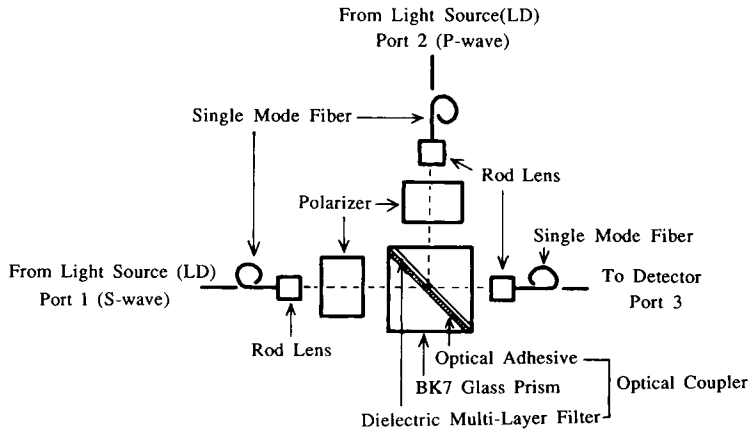


Figure 3 Loss deviation measuring system of optical coupler.

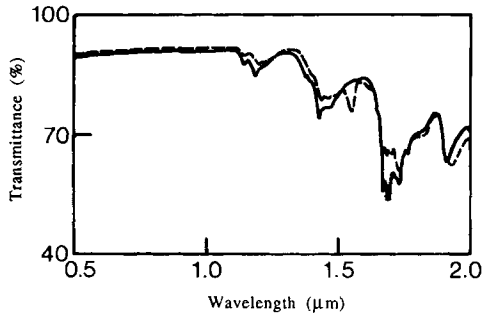


Figure 4 Transmittance spectra of polyether polyamine cured DGEBA and DGEBAF. Curing condition: 6-h cure at 65°C. Reference: Air. Contents (weight ratio): (—) DGEBA/Q694 = 100/40, (---) DGEBAF/Q694 = 100/40.

The refractive index in the near-infrared region was evalulated by return loss values because it could not be measured directly. Return loss (RL) from fused silica fiber/adhesive interfaces [Fig. 1(a)] is expressed by

$$RL = -10*\log[(n_f - n_a)^2/(n_f + n_a)^2] \quad (3)$$

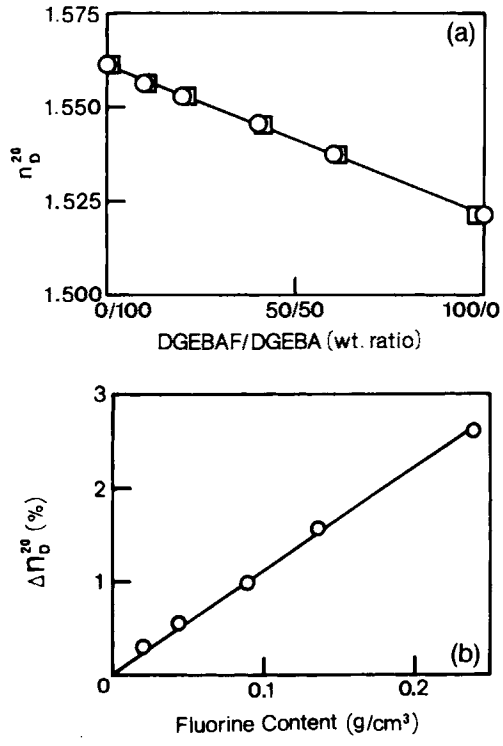


Figure 5 DGEBAF content dependence of refractive index in cured resin at 20°C (a) and fluorine atom content dependence of refractive index decreasing ratio (b). Curing agent content (weight ratio): (DGEBA + DGEBAF)/Q694 = 100/40. Curing condition: (a) 6-h cure at 65°C (○) and 4-h cure at 100°C (□); (b) 6-h cure at 65°C.

Table I Eisenlohr's Atomic Refraction and Covalent Bond Radius

Atom Type	Atomic Refraction	Covalent Bond Radius (Å)
H	1.10	0.30
F	1.24	0.72

where n_f and n_a are refractive indices of a fiber and an adhesive, respectively. Figure 6 shows the DGEBAF content dependence of RL values at $\lambda = 0.89$ and 1.30 μm. The RL values increase with DGEBAF content. RL values at 1.30 μm are slightly larger than those of 0.89 μm. Figures 5 and 6 show that the introduction of fluorine containing substituent lowers refractive indices of cured adhesives in a wide wavelength range from 0.59 to 1.30 μm.

Figure 7 shows changes in glass transition tem-

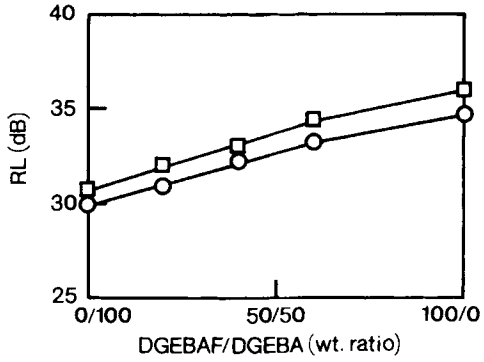


Figure 6 DGEBAF content dependence of return loss in adhesive terminated optical fiber. Curing agent content (weight ratio): (DGEBA + DGEBAF)/Q694 = 100/40. Curing condition: 6-h cure at 65°C. Wavelength: (○) 0.89 μm; (□) 1.30 μm.

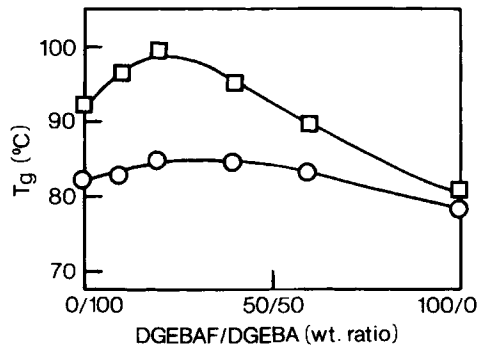


Figure 7 DGEBAF content dependence of glass transition temperature in cured resin. Curing agent content (weight ratio): (DGEBA + DGEBAF)/Q694 = 100/40. Curing condition: (○) 6-h cure at 65°C; (□) 4-h cure at 100°C.

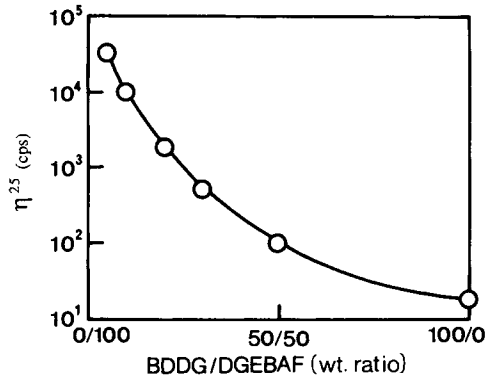


Figure 8 BDDG diluent content dependence of viscosity at 25°C in a BDDG and DGEBAF mixture.

perature (T_g) in the DGEBAF/DGEBA system. The high-temperature (100°C) cured resins show higher T_g values than the low-temperature (65°C) cured resins. In the DGEBAF system (DGEBAF/DGEBA = 100/0), however, the difference in T_g values between the curing temperatures becomes quite small. Even at a curing temperature as low as 65°C, the DGEBAF system shows high curability.

Diluent Effect

DGEBAF shows high viscosity values of more than 200,000 cps at 25°C. To obtain a homogeneous and formless mixture of DGEBAF with a curing agent, viscosities of epoxy resin must be diluted to less than 10,000 cps. Figure 8 shows the BDDG diluent content dependence of viscosity (η^{25}) in the DGEBAF/BDDG mixture. The η^{25} value is lowered by the diluent addition, and becomes less than 10,000 cps at BDDG contents of more than 10 wt %.

Figure 9 shows the temperature profiles of elastic modulus (E') in the cured DGEBAF system at various diluent contents. A flat region in E' is observed above the transition regions, by which the appearance of a rubbery state originating from crosslinking

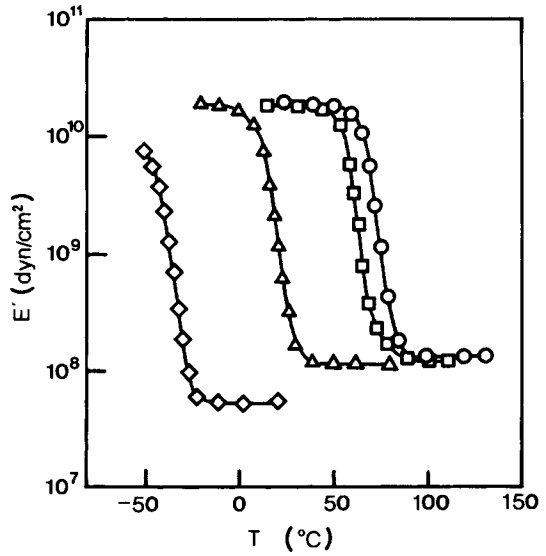


Figure 9 Temperature profiles of elastic modulus in cured DGEBA system at various diluent contents. Curing condition: 6-h cure at 65°C. Contents (weight ratio): (○) DGEBA/Q694 = 100/40, (□) DGEBAF/BDDG/Q694 = 80/20/40, (△) DGEBAF/BDDG/Q694 = 50/50/40, (◇) BDDG/Q694 = 100/40.

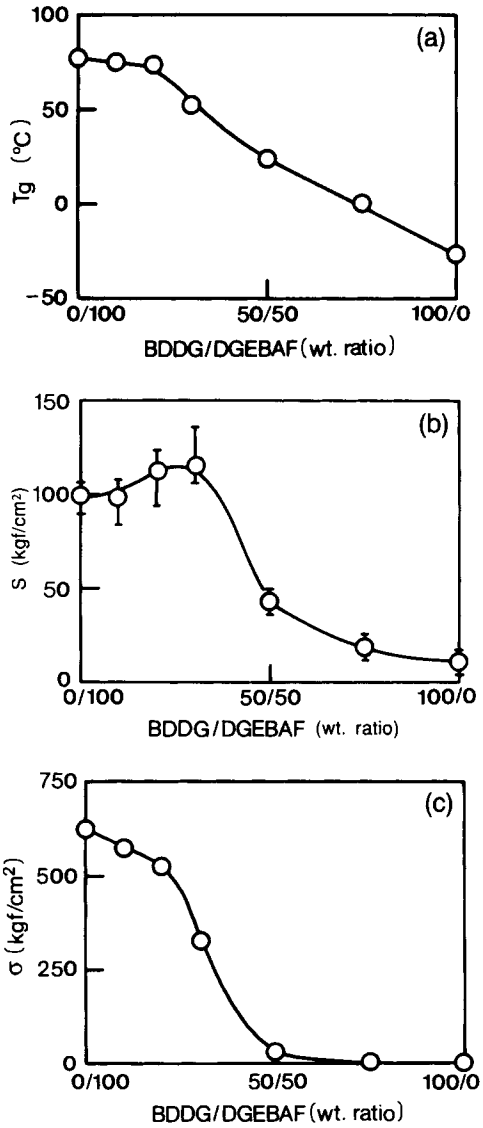


Figure 10 Diluent content dependence of glass transition temperature (a), tensile shear adhesive strength (b), and tensile strength (c) in cured DGEBA system. Curing agent content (weight ratio): (DGEBAF + BDDG)/Q694 = 100/40. Curing condition: 6-h cure at 65°C. Adherend: Copper.

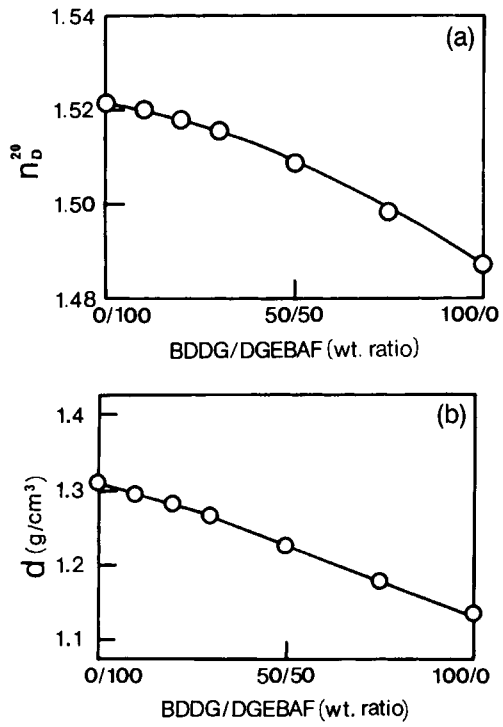


Figure 11 Diluent content dependence of refractive index at 20°C (a) and density (b) of cured resin. Curing agent content (weight ratio): (DGEBAF + BDDG)/Q694 = 100/40. Curing condition: 6-h cure at 65°C.

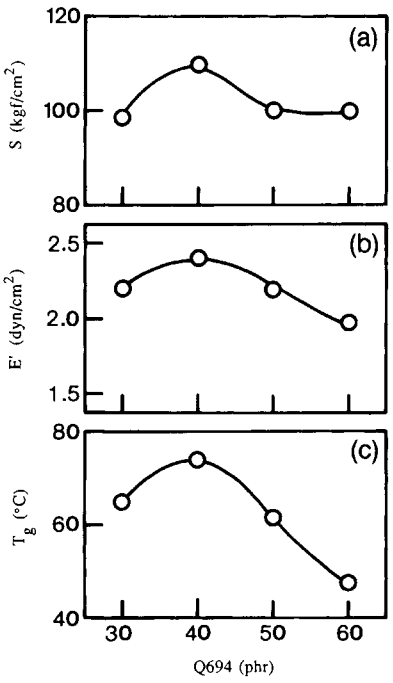


Figure 12 Curing agent content dependence of tensile shear adhesive strength (a), elastic modulus (b), and glass transition temperature (c). Curing condition: 6-h cure at 65°C. Adherend: Copper. Epoxy content (weight ratio): DGEBAF/BDDG = 60/40.

structures in cured resigns is confirmed. The crosslinking density of a thermosetting polymer is generally expressed by[8,9]

$$E'_{rub} = 3\phi\rho RT \quad (4)$$

where ϕ is the front factor, ρ is the crosslinking density, R is the gas constant, and T is the absolute temperature. The decrease in E'_{rub} (Fig. 9) in a high diluent content system exhibits a decrease in ρ in the cured resins.

The diluent content dependencies of T_g, tensile shear adhesive strength (S), and tensile strength (σ) are shown in Figure 10. The decreases in T_g and σ and the increase in S are very slight for diluent contents up to 30 wt %, although these values drastically decrease with diluent addition of more than 30 wt %. Both S and σ remain at low values in a rubbery region of the DGEBAF system. The diluent content dependence of n_D^{20} and density are shown in Figure 11. The n_D^{20} value of the DGEBAF system decreases with diluent content increase. In this case, the blend of low refractive index diluent causes the decrease in [R] in eq. (2), and the decrease in density generates an increase in V. The resulting decrease in [R]/V induces a gradual reduction in n_D^{20} with increasing diluent content. Figures 10 and 11 clarify that there are slight changes in the properties of cured resins in the diluent content region of less than 30 wt %. The maximum temperature of optical devices reaches 60°C in practical optical communications systems, and the optical adhesive must show stable properties at ambient temperatures. In the BDDG/DGEBAF system, therefore, BDDG diluent content must be 20 wt % to maintain a T_g value higher than 60°C.

Figure 12 shows the curing agent content dependence of S, E', and T_g. The maximum values are obtained at curing agent contents of 40 parts per hundred resins (phr). These results show that the

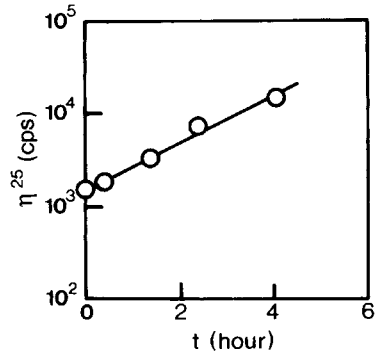


Figure 13 Time dependence of the viscosity at 25°C in the mixed F–OA system.

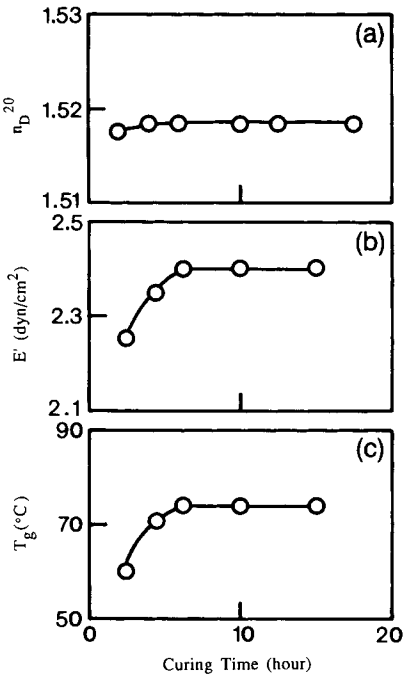


Figure 14 Curing time dependence of refractive index (a), elastic modulus (b), and glass transition temperature (c) of the F-OA system. Curing temperature: 65°C.

optimized fluorine-containing optical adhesive composition, called the F-OA system, contains DGEBAF, BDDG, and Q694 in a weight ratio of 80 : 20 : 40.

Properties of Formulated Optical Adhesive Composition

Figure 13 shows the time dependence of the η^{25} value of the F-OA system after mixing DGEBAF, BDDG, and Q694. Although the η^{25} value gradually increases

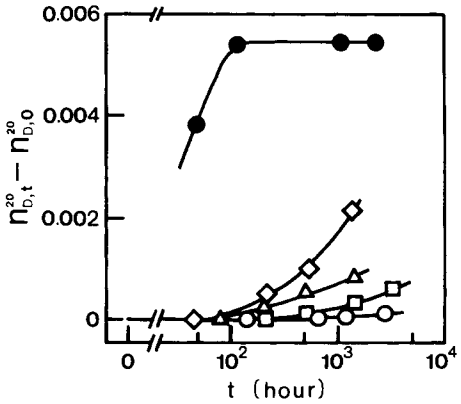


Figure 15 Time dependence of refractive index of F-OA and C-OA. F-OA: (○) 65°C; (□) 80°C; (△) 100°C, (◇) 120°C. C-OA: (●) 65°C.

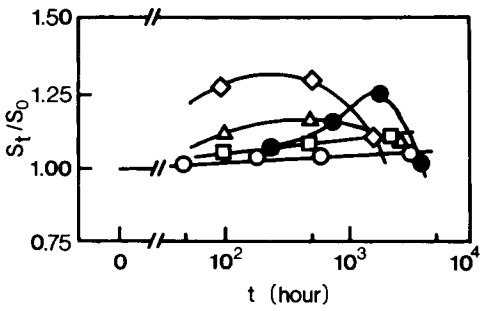


Figure 16 Time dependence of tensile shear adhesive strength of F-OA and C-OA. F-OA: (○) 65°C; (□) 80°C; (△) 100°C; (◇) 120°C. C-OA: (●) 65°C.

with retention time, it remains less than 5,000 cps even after 2 h. The F-OA system, therefore, gives good workability due to its long pot life. Figure 14 shows the curing time dependence of n_D^{20}, E', and T_g of the F-OA system. E' and T_g increase with curing time, and reach constant values after 6 h. The curing time of 6 h is sufficient to cure this adhesive composition.

The time dependence of indices of the F-OA and a conventional adhesive C-OA are shown in Figure 15. The n_D^{20} value (initial refractive index, $n_D^{20}{}_0 = 1.518$) of the F-OA scarcely changes after aging at 120°C for 1000 h. On the other hand, the n_D^{20} value of the conventional optical adhesive significantly increases after low-temperature aging as low as 65°C.

Figure 16 shows the time dependence of tensile shear adhesive strengths. The S value of F-OA does

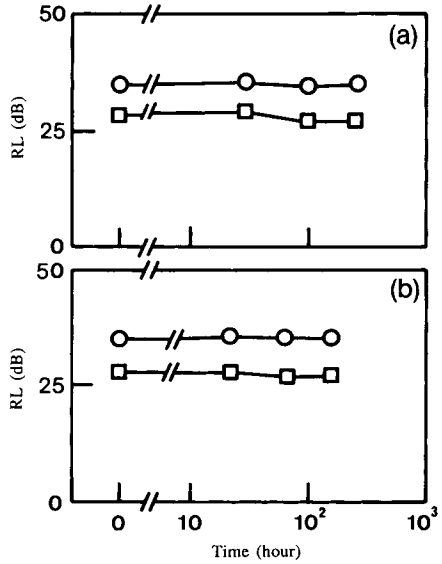


Figure 17 Aging time dependence of return loss in fiber end samples at 75°C (a) and at 85°C and 95% RH (b). Wavelength: 1.30 μm. (○) F-OA; (□) C-OA.

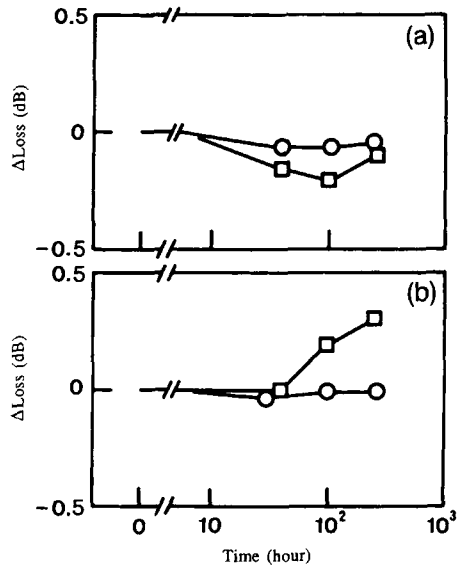


Figure 18 Aging time dependence of loss deviation in filter model samples at 75°C (a) and at 85°C and 95% RH (b). Wavelength: 0.89 μm. (○) F-OA; (□) C-OA.

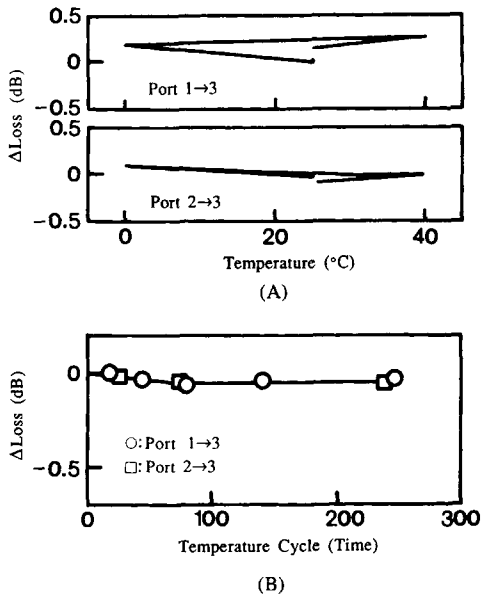


Figure 19 Temperature characteristics (a) and temperature cycle characteristics (b) of optical couplers fabricated with F-OA. Temperature profile: (a) 25°C → 0°C → 40°C → 25°C; (b) (5°C, 30 min) + (5°C → 50°C, 30 min) + (50°C, 30 min) + (50°C → 5°C, 30 min). Measuring temperature: (b) 5°C.

not change after 65°C aging, but that of the conventional optical adhesive increases with the progress of after-curing. These results indicate that the F-OA system has high heat durability.

Properties of Adhered Parts in Devices

Figure 17 shows the aging time dependence of RL in fiber end samples [Fig. 2(a)]. The RL value with the F-OA exhibiting a low refractive index is higher than that of C-OA, i.e., light reflection is relatively low in F-OA. Figure 18 shows the aging time dependence of loss deviations in filter samples [Fig. 2(b)]. The loss deviation with the F-OA system is low, changing much less than that of the C-OA system. The temperature characteristics and the temperature cycle characteristics of optical couplers fabricated with F-OA are shown in Figure 19. The loss deviation is within 0.25 dB in a temperature range of 0–40°C, with up to 200 temperature cycles.

In conclusion, the use of F-OA as an optical adhesive can reduce reflection loss by refractive index matching with optical glass such as BK7 and fused silica. The reliability of optical devices such as LD modules, APD modules and optical couplers has been improved in practice, and these devices have been applied to a submarine light transmission system,[2] etc.

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