Synthesis and Properties of a Novel Fluorine-Containing Alicyclic Diepoxide

T. Maruno,* K. Nakamura, and N. Murata

NTT Interdisciplinary Research Laboratories, 3-9-11, Midori-cho, Musashino-shi, Tokyo 180, Japan

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ABSTRACT: A novel fluorine-containing alicyclic diepoxide resin, the diglycidyl ether of bis(1,1,1,3,3,3-hexafluoropropyl)cyclohexane (CHEP), has been synthesized using benzene, hexafluoroacetone, and epichlorohydrin. The CHEPs, consisting of a mixture of 1,3- and 1,4-isomers, whose epoxy equivalent weights are 270 and 290, are liquids with viscosities of 5000 and 30 000 cP at 25 °C, whereas the 1,4-isomer CHEP is a solid resin. The liquid CHEPs show low refractive indexes of ∼1.405 due to the high fluorine content of more than 43 wt %. They also show high optical transparency to UV because they are nonaromatic hydrocarbons. The CHEPs can be cured by heat or UV irradiation in the presence of curing agents. The cured resins show refractive indexes of less than 1.45, and a 1-mm-thick film has a high transparency of more than 80%, which includes Fresnel's reflection loss at both sides of the film/air interfaces, at wavelengths from 0.5 to 1.6 μm. The glass transition temperature is up to 53 °C, and tensile shear strength to quartz glass is more than 100 kg/cm^2.

Introduction

The development of photonics and microoptoelectronics has created a strong need for transparent organic materials. These materials are suitable for molding lenses and prisms and for joining optical components to other components.[1−5] Epoxy resin compositions are widely used for molding resins and adhesives. It is particularly important to be able to control the refractive index of optical resins in order to match them with optical components. We previously reported new optical adhesive compositions containing a fluorinated epoxy resin[6−8] and have shown that the fluorination of epoxy resins is a practical method of controlling refractive index. However, conventional epoxy resins are still high in refractive index (1.51−1.58 at 0.59-μm wavelength), so they cannot be matched with low-refractive-index optical components such as quartz prisms and optical fibers (refractive indexes are ∼1.46).

In optical device fabrication processes, low-temperature curability and rapid curability are needed for resins to prevent degradation of neighboring materials. Low viscosity and long pot life are also required for good workability. UV initiators have recently been developed for epoxy resin systems to obtain a long pot life and rapid curing at low temperature.[9−11] Conventional Bisphenol-A type resins, however, absorb UV light due to their aromatic rings and show low UV curability. Aliphatic epoxy resins have therefore been examined for UV-curable resin systems due to their high transparency to UV light, but heat durability and adhesive strength were not sufficient because of their flexible main-chain structure.[12]

The investigation reported here was to obtain an epoxy resin with low refractive index, high optical transparency from UV to near-infrared, high adhesive strength, and high heat resistance. In order to improve these properties, we tried to introduce an alicyclic group and a fluorinated group into the epoxy resin. We therefore prepared a novel fluorine-containing alicyclic diepoxide resin, the diglycidyl ether of bis(1,1,1,3,3,3-hexafluoropropyl)cyclohexane (CHEP), which is synthesized from benzene, hexafluoroacetone, and epichlorohydrin (Scheme 1). In addition to the synthesis, we discuss the properties of uncured and cured CHEP.

Experimental Section

Materials. The chemical agents **I**−**VII** in Scheme 1 were synthesized as follows.

Preparation of Bis(1,1,1,3,3,3-hexafluoro-2-hydroxyisopropyl)benzene (I). Benzene (117 g, 1.5 mol) and 31 g (0.23 mol) of anhydrous aluminum chloride were placed in a 1-L flask equipped with a stirrer. Hexafluoroacetone (500 g, 3 mol) was introduced at a rate of ∼5 g/min at room temperature with stirring. The reaction mixture was distilled at a reduced pressure to obtain 517 g (1.26 mol) of **I**, which is a mixture of meta and para isomers in 85:15 mole ratio. The boiling point of **I** is 102−106 °C at 20 mmHg. The yield based on hexafluoroacetone is 84%.

Preparation of Bis(1,1,1,3,3,3-hexafluoro-2-hydroxyisopropyl)cyclohexane (II, III). A mixture of 2-propanol (300 mL) and 300 g (0.73 mol) of **I** was placed in a Hastelloy autoclave. Rhodium (30 g) supported by carbon powder (catalyst, rhodium content, 5% by weight based on the total weight) was added to the mixture. The mixture was heated at 155 °C with stirring and then pressurized at 60 kg/cm^2 with hydrogen and reacted for 4.5 h. The reaction mixture was cooled to room temperature, and 2-propanol was removed by distillation after separating the catalyst-supporting carbon powder. The residue was distilled at a reduced pressure to obtain 287g (0.69 mol) of **II**. The boiling point of **II** was 96−100 °C at 6 mmHg and its yield was 94%. Gas chromatographic analysis showed that **II** consists of a mixture of 1,3- and 1,4-isomeric diols with 85:15 weight ratio. The isomer mixture **II** was cooled at 10 °C for 1 week to crystallize the 1,4-isomer. The precipitated crystals were filtered and washed with trichlorotrifluoroethane to obtain 26 g (0.063 mol) of **III**. ^{1}H NMR (in CCl_4, TMS standard, δ ppm): 1.1−2.5 (10H, br, alicyclic CH and CH_2), 3.1 (2H, s, OH).

Preparation of Diglycidyl Ether of Bis(1,1,1,3,3,3-hexafluoroisopropyl)cyclohexane (IV−VII). Sodium hydroxide (16.8 g, 0.42 mol) and 2 mL of water were added to a mixture of 382 g (4.13 mol) of epichlorohydrin and 86 g (0.21 mol) of **II**. The mixture was heated with stirring and reacted with refluxing for 10 h. The resulting sodium chloride was removed by filtration with a glass filter, and the excess of epichlorohydrin was distilled off under reduced pressure. The residue was analyzed by gel permeation chromatography (GPC) using a Shodex KF-801 and KF-802 (Showa Denko Co.) column series and chloroform solvent. This showed that the

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* To whom correspondence should be sent. E-mail: maruno@aela.ntt.jp.

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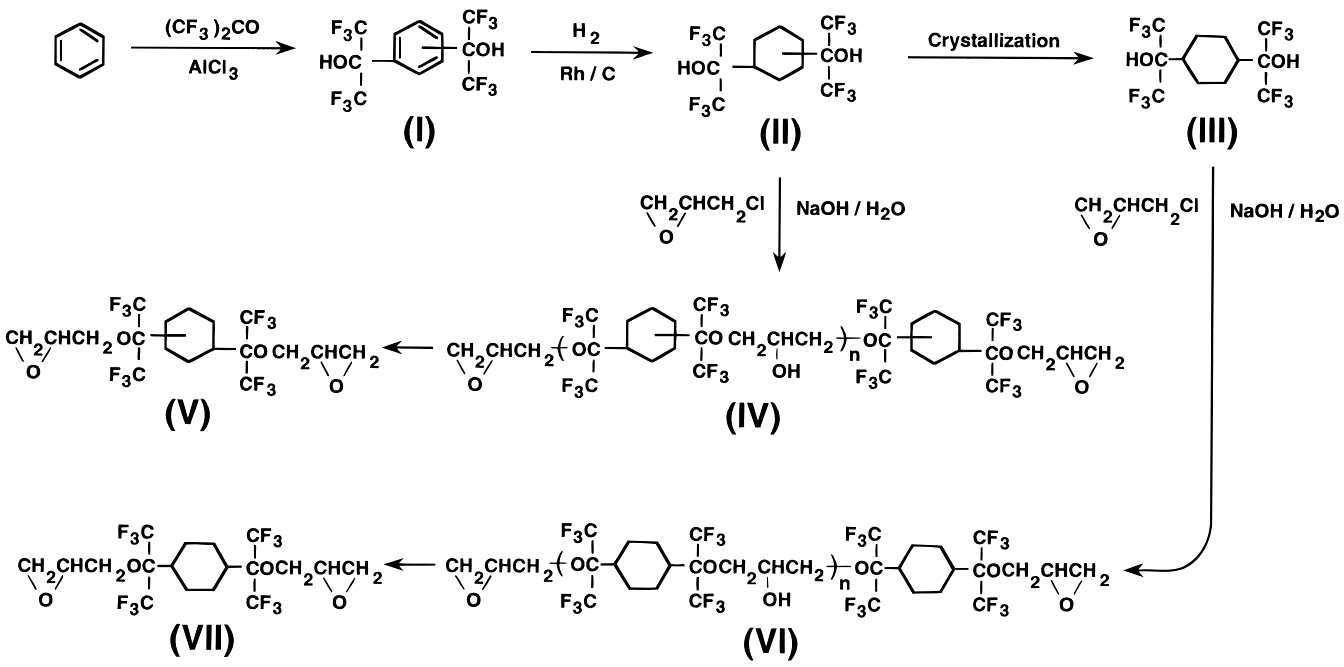
Scheme 1



n values of 0, 1, and ≥2 in **IV** were in the ratio 93:6:1 (ratio of areas on the chromatogram). The residue was distilled to obtain 50 g of $n = 0$ **V**. The ether **V** had a boiling point of 138–150 °C at 1 mmHg. **VI** was prepared by the reaction of **III** and epichlorohydrin in the same manner as the **IV** preparation and distilled to obtain $n = 0$ **VII**. The ether **VII** had a boiling point of 147–151 °C at 1 mmHg. Epoxy equivalent weights (EEW), which were measured by the HCl–pyridine method, of **IV**–**VII** were 290, 270, 318, and 272, respectively. ^{1}H NMR of **V** and **VII** (in $CDCl_3$, TMS standard, δ ppm): 1.3–2.3 (10H, br, alicyclic CH and CH_2), 2.6, 2.8 (4H, m, $H_2\overset{\ulcorner O \urcorner}{C{-}C}{-}$), 3.2 (2H, m, $\overset{\ulcorner O \urcorner}{C{-}CH}{-}$), 3.7, 3.9 (4H, m, $\overset{\ulcorner O \urcorner}{C{-}C}CH_2{-}$).

The diglycidyl ether of bis(1,1,1,3,3,3-hexafluoroisopropyl)benzene (BZEP) and 2,2,3,3-tetrafluoropropyl glycidyl ether (PRGE) were synthesized by previously reported methods.[13–17] The fluorine atom contents of BZEP and PRGE were calculated to be 44 and 40 wt %, respectively. The diglycidyl ether of Bisphenol A (AEP, Epikote 828) was obtained from Yuka Shell Epoxy Co. Ltd. The EEW of AEP was 189 and n_D^{20} was 1.574. The 1,6-hexanediol diglycidyl ether (HDDE, Denacol EX-212) was purchased from Nagase Chemical Ltd. as a low-viscosity diluent. The EEW of HDDE was 150 and the viscosity at 25 °C, η^{25}, was 20 cP. The 1,4-butanediol diglycidyl ether (BDDE, Aldrich Chemical Co. Inc.) was also used as a diluent.

An aliphatic polyether polyamine (PEPA, EPOMIC Q694, Mitsui Petrochem. Ind. Epoxy Corp.) was used for curing epoxies by heat. The value of active hydrogen equivalent weight of PEPA was 80, n_D^{20} was 1.461 and η^{25} was 76 cP. PEPA was added 40 parts by weight per hundred epoxy resin (phr) for curing. Monoethylamino trifluoroborate (MEA, Nakarai Chemicals), which is a semilatent catalyst for epoxies, was also used as a heat curing agent. Triarylsulfonium salt (TAS, UV-6970, Union Carbide Co.) was used as a UV curing catalyst. Both catalysts, MEA and TAS, were added 2–5 phr for curing.

Cured Sample Preparations. CHEP showed poor solubility when TAS curing agent was used. Therefore, the maximum CHEP content in the formulation of UV-curable epoxy was controlled to less than 70 wt % by mixing with other epoxies. These conditions prevent precipitation of TAS. Before preparing the cured sample, trapped gas in the stirred mixture of the epoxy resin and the curing agent was entirely removed by heating in a vacuum oven for 5 min to prevent the appearance of voids in the cured resins. The oven temperature was 25–40 °C and the pressure was ~1 mmHg. Heat curing conditions were 6 h at 65 °C for the PEPA curing agent and 3 h at 120 °C for the MEA. UV irradiation for the TAS curing catalyst was carried out with a high-pressure Hg lamp at 10 mW/cm^2 for 10 min.

Sheet samples 1 mm thick were prepared by the casting method. They were cut into 10 × 10 × 1 mm^3 pieces for refractive index measurement and 25 × 10 × 1 mm^3 for light transmission loss measurement. Quartz plates, 20 × 35 × 5 mm^3, were used to prepare single lap joints for tensile shear strength tests. Lapping length was 10 mm.

Measurements. The NMR spectra were measured with a Brucker MSL-400 NMR spectrometer, using CCl_4 and $CDCl_3$ solvents. The IR spectra were measured with a Perkin-Elmer 2000 spectrometer. Light transmission loss from UV to near-IR was measured with a spectrometer (Hitachi U-3500). Refractive indexes were measured at 20 °C with an Abbe refractometer (Atago Co. Ltd., Tokyo). Viscosity was measured at 25 °C with a B-type viscometer (Tokyo Precision Instrument Co. Ltd.). Gas chromatography (GC) was conducted using a Type-163 (Hitachi) gas chromatography. GPC was done with a Hitachi LC3A liquid chromatograph. The GPC was conducted using a series of Shodex KF-801 and KF-802 columns, and the solvent was chloroform. Glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) with a Perkin-Elmer TAS-7 differential scanning calorimeter. The DSC measurement was done with a heating rate of 10 °C/min under a nitrogen atmosphere. Tensile shear strengths were measured at 5 mm/min cross-head speed and at 23 °C by an Instron Universal Tester.

Results and Discussion

Properties of Uncured CHEP. The CHEP was synthesized by the reaction of diol **II** and epichlorohydrin as shown in Scheme 1. The diol **II** was obtained with 84% yield based on hexafluoroacetone. Howard et al.[18] previously reported that cyclohexane and hexafluoroacetone react together in the presence of free-radical initiators or ultraviolet irradiation to give a mixture of isomeric diols **II**. The yield of **II** in the radical reaction, however, remains less than 20%. On the other hand, the reaction in Scheme 1 readily gives **II** with good yield based on hexafluoroacetone because it consists of a Friedel–Crafts reaction of benzene and hexafluoroacetone followed by hydrogenation to **I**. Each CHEP was identified by NMR and IR. Figure 1 shows the NMR spectrum of **V** as an example. Five peaks appeared at

Table 1. Characteristics of CHEPs

CHEP	bp (°C/mmHg)	isomer (wt %) 1,3	isomer (wt %) 1,4	*n* dispersion (%) $n = 0$	*n* dispersion (%) $n = 1$	*n* dispersion (%) $n \geq 2$	viscosity (cP)	EEW (g/equiv)	refractive index	F atom content (%)
IV		85	15	93	6	1	30,000	290	1.408	43.4
V	138−150/1	85	15	100	0	0	5,000	270	1.405	43.2
VII	147−151/1	0	100	100	0	0	solid	272		43.2

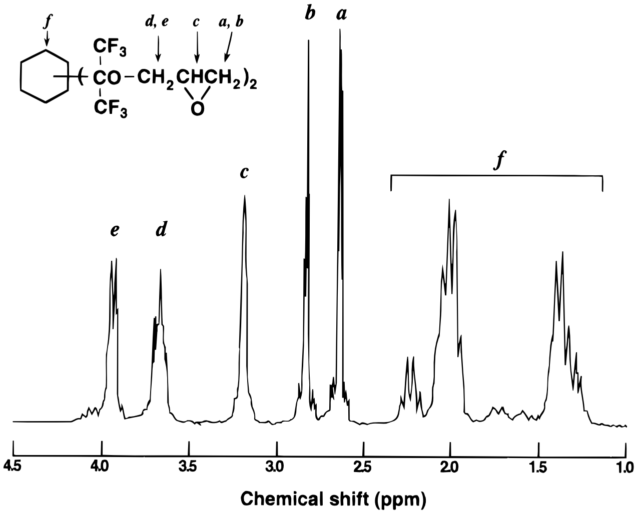


Figure 1. ^{1}H-NMR spectrum of CHEP **V**. Solvent, $CDCl_3$; standard, TMS.

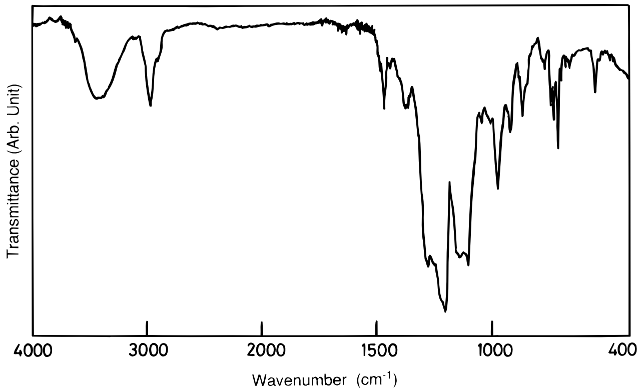


Figure 2. IR spectrum of CHEP **IV**.

2.6, 2.8, 3.2, 3.7, and 3.9 ppm and were assigned to the chemical shifts of the glycidyl group in CHEP. Protons in the cyclohexane ring show broad peaks at 1.3−2.3 ppm. Almost the same NMR behavior was observed for the other CHEPs. Figure 2 shows the IR spectrum of **IV**, as an example. This CHEP showed characteristic absorption peaks at 914 cm^{-1} due to the epoxy ring and at 1209 cm^{-1} due to trifluoromethyl groups. Therefore, the synthesis of CHEPs was also followed by IR spectra.

The properties of the CHEPs synthesized are listed in Table 1. CHEPs **IV** and **V** contain 1,3- and 1,4-isomers with the weight ratio of 85:15 and are liquid resins with viscosity values as low as 5000 and 30 000 cP at 25 °C. The CHEPs **VI** and **VII**, which consist of only 1,4-isomer, are solid resins at the same temperature. The average *n* values of 0.1 for **IV** and 0.2 for **VI** were obtained from the aforementioned GPC data. Distilled CHEPs **V** and **VII** were composed of $n = 0$ compound as observed by GPC and showed EEW values of 270 and 272, respectively, which are approximately equal to the calculated value for $n = 0$ (EEW = 264). It is clearly observed that the $n = 0$ component can be easily separated by the distillation of CHEP. The fluorine content was calculated using these *n* values.

Table 2. Atomic Refraction, Increment for Bond Type, and Covalent Bond Radius

atom and bond type	atomic refraction, increment for bond type	convalent bond radius (Å)
−H	1.10	0.30
−F	1.24	0.72
⟩C⟨	2.42	
double bond	1.30	

Table 3. Characteristics of Benzene, Cyclohexane, BZEP, and CHEP V

agent	MW	density, d_4^{20}	refractive index, n_D^{20}	mol vol (cm^3)	molar refraction
benzene	78.11	0.879	1.501	88.86	26.2
cyclohexane	84.16	0.778	1.426	108.2	27.7
BZEP	522.3	1.625	1.433	321.4	83.5
CHEP **V**	528.3	1.517	1.405	348.3	85.4

The refractive indexes of the CHEPs (e.g., the lowest value of $n_D^{20} = 1.405$ for **V**) are much lower than that of nonfluorinated AEP (1.574). They were also lower than that of BZEP (1.433), which is an aromatic analog of CHEP and contains 44 wt % fluorine atoms. The refractive index (*n*) of an organic material is generally expressed by the Lorents−Lorens equation:

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

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 larger [*R*] and *V* values than hydrocarbons because of the larger values of atomic refraction and covalent bond radius of the fluorine atom than those of a hydrogen atom as shown in Table 2. Fluorine substitution causes a large increase in *V* rather than [*R*] because the increase in radius is larger than that of atomic refraction. The CHEPs and BZEP, therefore, show low n_D^{20} compared to that of nonfluorinated diepoxy resin such as AEP (n_D^{20} = 1.574). The difference in n_D^{20} between CHEPs and BZEP is due to the difference between alicyclic and aromatic rings because the C−C bond has a lower atomic refraction than the C=C bond. The [*R*] values of benzene, cyclohexane, BZEP, and CHEP **V** were calculated using eq 1 and are listed in Table 3 with *d*, *M*, and *V* values. Hydrogenation of the aromatic ring in BZEP generates the increases of [*R*] and *V*. The decrease in n_D^{20} of CHEPs, which results from a decrease in [*R*]/*V*, indicates that the hydrogenation strongly affects the increase in *V*.

Figure 3 shows the transmission spectra of liquid CHEP **IV** and AEP. Optical path length was set to be 1 mm using a quartz glass sample cell and a 2-mm-thick quartz plate, which is the same thickness as both sides of the sample cell, was used as a reference. The light transmission of epoxies decreases at wavelengths below 0.35 μm. The wavelengths of 50 and 90% absorption of CHEP are 284 and 269 nm. On the other hand, those of AEP are 311 and 307 nm. This strong absorption of AEP is caused by the π−π* transition of aromatic hydrocarbons. High UV transparency is obtained in CHEP because it consists of nonaromatic hydrocarbons.

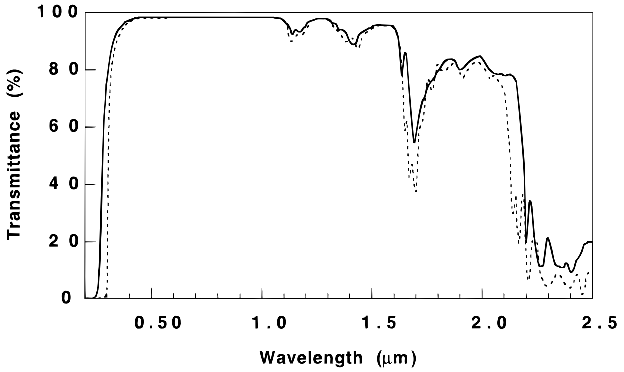


Figure 3. Transmission spectra of liquid CHEP **IV** and AEP. Optical path length, 1 mm; reference, 2-mm-thick quartz glass plate.

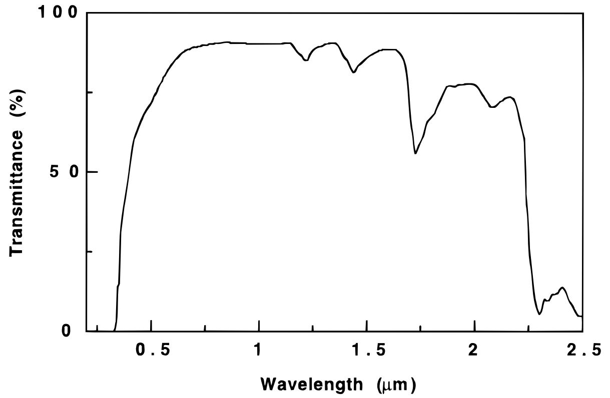


Figure 4. Transmission spectra of UV-cured CHEP of 1 mm thickness. Contents (weight ratio), CHEP/HDDE/TAS = 70: 30:2.

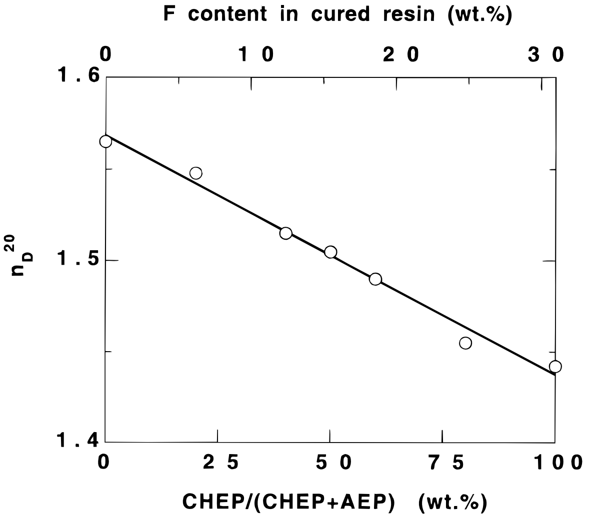


Figure 5. Dependence of refractive index at $\lambda = 0.59$ μm (n_D^{20}) on CHEP content in cured resin. Contents (weight ratio), (CHEP + AEP)/PEPA = 100:40.

Therefore, CHEP should be advantageous in formulating UV-curable epoxy resins.

Properties of Cured CHEP. Optical transparency is an important factor because resins are often used to fabricate light-transmission paths in photonic and microoptoelectronic devices. Figure 4 shows transmission spectra of UV-cured CHEP. The thickness of the cured film was 1 mm and the reference was air. Therefore, the spectrum in Figure 4 contains Fresnel's reflection loss, RL, at both sides of the film/air interfaces according to the following:

$$\mathrm{RL} = (n - 1)^2/(n + 1)^2 \qquad (2)$$

where n is the refractive index of the cured sample. At near-IR wavelengths, there are some absorption peaks due to the harmonics and their coupling of stretching (ν) and deformation (δ) vibrations of C−H bonds. Three absorption peaks at 1.65, 1.4, and 1.1 μm wavelength were assigned to the $2\nu_{CH}$, $2\ \nu_{CH} + \delta_{CH}$, and $3\ \nu_{CH}$ bands, respectively.[19] Cured CHEP showed a sufficiently high transmittance value of more than 80% in the wavelength range of 0.5−1.6 μm, which is usually used for optical devices and optical communication. Transmittance at UV wavelengths was shifted to longer wavelengths (~350 nm) by curing because of the absorption of the UV curing agent.

Figure 5 shows how the refractive index at $\lambda = 0.59$ μm (n_D^{20}) depends on CHEP content in PEPA cured resins. The n_D^{20} value decreases linearly with increase in CHEP content and reaches 1.442 in CHEP cured with PEPA. This value is lower than that of quartz glass fiber used in optical communication systems (~1.46). These results show that the refractive index can be controlled to match the neighboring materials by changing the fluorine content in cured resin, thus minimizing the reflection loss at the interface.

Typical formulations and properties of cured resins are listed in Table 4. The cured CHEPs show lower refractive indexes than AEP and BZEP due to high fluorine content and nonaromatic structure. Lower refractive indexes were observed in catalytic curing agent systems because both MEA and TAS were added in small amounts and the fluorine contents of cured samples are more than 40%. The T_g of CHEP remains slightly lower than that of BZEP. This fact shows that the decrease in rigidity in the CHEP chain, which is caused by the aliphatic substitution into BZEP, is very slight. Moreover, CHEP formulations show sufficiently high tensile shear strength values of more than 100 kg/cm^2. These results show that cured CHEP has a low refractive index, high T_g, and high adhesive strength. Therefore, formulations containing CHEP are promising candidates for adhesives in photonic devices and microoptoelectronic devices.

Table 4. Contents and Properties of Cured Epoxy Resin

epoxy resin	wt %[a]	diluent epoxy	wt %[a]	curing agent	phr[b]	F atom (wt %)	refractive index n_D^{20}	tensile shear strength (kg/cm^2)	T_g (°C)
CHEP	100			PEPA	40	31	1.442	>190	53
	80	PRGE	20	PEPA	40	30	1.444	110	34
	85	PRGE	15	MEA	5	41	1.417		42
	70	PRGE	30	TAS	3	41	1.431	156	
BZEP	100			PEPA	40	31	1.453	>150	62
AEP	80	BDDE	20	PEPA	40	0	1.564	110	70

[a] Weight percentage in total epoxy resin. [b] Parts by weight per hundred epoxy resin.

Conclusions

We have prepared a novel fluorine-containing alicyclic diepoxide resin, the diglycidyl ether of CHEP. The CHEPs that consist of a mixture of 1,3- and 1,4-isomers, whose epoxy equivalent weights are 270 and 290, are liquids with viscosity of 5000 and 30 000 cP at 25 °C, whereas the 1,4-isomer CHEP is a solid resin. The liquid CHEPs have low refractive indexes of ~1.405 due to a fluorine content of more than 43 wt %. They also have high optical transparency in UV because they are alicyclic hydrocarbons. These CHEPs can be cured by heat or UV irradiation in the presence of curing agents. The cured resins have refractive indexes of less than 1.45, and a 1-mm-thick film has high transparency of more than 80% in the wavelength range from 0.5 to 1.6 μm. The glass transition temperature is up to 53 °C, and tensile shear strength to the quartz glass are more than 100 kg/cm^2.

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