We investigated the formulations of epoxy resins which were used with deep-UV LED lamps. The mixtures of epoxy monomers and photoacid generators (PAGs) were placed on a silicon wafer to form films. The films were irradiated by deep-UV lamps which emit 265, 285 or 300-nm light. The effects of the PAGs, irradiation wavelengths, and film thicknesses on the reactivity were investigated by FT-IR spectroscopy and a photo-DSC study. We found that a sulfonium salt having a thiophenyl moiety was the most effective PAG. We also found that less than 100-μm thick films were effectively cured by irradiation from the deep-UV LEDs.

Keywords: Photocuring, Deep-UV LED, Epoxy, Photoacid generator

1. Introduction

The photocuring of epoxy resins [1-6] has been extensively studied due to the wide applicability, such as negative-type photoresists, coating materials and printing materials, to overcome the oxygen inhibition of the photocuring system using acrylates [1]. We are strongly interested in UV light-emitting diodes (UV LEDs) as the light sources for UV-curing technologies due to their long life, high stability, bright output, compactness, and low power requirement. The rapid development of UV LED technologies, especially the extension of deep UV regions [7-13], encourages us to investigate the application of a cationic photocuring system such as photoacid generators (PAGs) [14-19] and photosensitizers [20,21]. From this point of view, we investigated the formulations of photocurable acrylate resins applicable to deep UV LED lamps which emit 265, 285 or 300-nm light [13]. We reported the formulations of acrylates which can be used in deep UV LED lamps. We found that the irradiation by a deep UV LED can effectively suppress the oxygen inhibition for less than several micrometer-thick films containing photoinitiators including O-benzoyl 2,3-butanedione monooxime [22].

Based on these findings, we have extended the previous work to cationic photopolymerization using PAGs and an epoxy compound. The mixtures of the epoxy compound and PAGs were irradiated by deep UV lamps which emit 265, 285 or 300-nm light. The effect of the PAGs, irradiation wavelength, and sample thickness on the conversion of the epoxy unit was discussed by FT-IR spectroscopy and photo-DSC measurements.

2. Experimental

2.1. Materials

The structures of the used chemicals were shown in Fig. 1. An epoxy monomer, 3,4-epoxycyclohexymethyl 3,4-epoxycyclohexancarboxylate (ERL-4221, Union Carbide Japan) and PAGs, bis(4-tert-butylphenyl)iodonium hexafluorophosphate (DIP, TCI Japan), tris(4-methylphenyl)sulfonium hexafluorophosphate (TTSP,
TCI Japan), diphenyl[(4-phenylthio)phenyl]sulfonylum hexafluorophosphate (DPTPSP, CPI-100P, San Apro, Japan), and 8-(tert-butyl-5-(4-methoxyphenyl)-1,3-dioxo-1H-[1,4]benzodithiino[2,3-f]-isoindolium hexafluorophosphate [23] (THIP, SIN-02, Sanbo Chemical, Japan) were used as received.

Fig. 1. Structures of chemicals used.

2.2. Method

Commercially-available deep-UV LED lamps (SMD series: 265, 285 and 300 nm) from Nikkiso Giken (Ishikawa, Japan) were used as the light sources. An array of 2 x 12 LED packages was placed on a board with a heat sink within the area of a 3 cm x 10 cm rectangle as the light sources. The light intensities of the deep UV LEDs upon irradiation at 265, 285 and 300 nm were 0.28, 0.74 and 0.70 mW/cm², respectively.

Irradiation was also performed using a medium pressure mercury lamp (Hamamatsu Photonics, Lightningcure LC8, 280 W) without a filter and a Xenon lamp (Asahi Spectra, MAX-301, 300 W) through band-path filters at 254, 285, 300 or 365 nm combined with a mirror which passes the light below 400 nm using a Shimadzu UV-DSC system in air or N₂. Conversion of the epoxy unit in the blended film was determined using the heat value of 94.5 kJ/mol for one reacted epoxy group [24].

2.3. Measurement

The FT-IR measurements were carried out using a JASCO FT/IR-4600. The UV-vis spectra were obtained by a Shimadzu UV-2600. The intensity of the light was measured by an Orc Light Measure UV-M02 or Ushio USR-45VA. The thickness of the films was determined using a Nanometrics M3000 interferometer or a peacock dial thickness gauge (model G, OZAKI MFG.).

3. Results and discussion

3.1. Characteristics of PAGs and light sources

Photocuring is generally achieved by photopolymerization which is obtained by the utilization of PAGs and photopolymerizable agents. PAGs are key materials for the cationic UV-curing processes. The first stage of the UV curing system is the absorption of a photon from the incident radiation by the PAGs. The PAGs generate acids by light absorption from the light sources. Thus, the absorption spectra of the PAGs are quite important when selecting the PAGs.

In this study, we selected four compounds of the PAGs, which generate hexafluorophosphoric acid; one of the useful acids for photopolymerization of the epoxy units. The effect of the structures of the PAGs can be evaluated by the reaction rate of the epoxy units. Figure 2 shows the UV-vis spectra of the PAGs in acetonitrile.

In this study, we investigated the deep UV LEDs at 265, 285 and 300 nm in addition to the 365-nm light and medium pressure mercury lamp which has multiple line spectra as a
conventional light source. We used the same light sources described in a previous paper [13].

![Figure 2](image2.png)

**Fig. 2.** UV-vis spectra of DIP (bold line), TTSP (dotted line), DPTPSP (solid line), and THIP (broken line) in acetonitrile (1.0 x 10⁻⁴ M).

3.2. Photocuring behavior

The photocuring behaviors were investigated using photo-DSC measurements. The thickness of the samples was adjusted to 200 μm due to the limitation of the photo-DSC instrument. The concentrations of the PAGs in the ERL-4221/PAGs (1:0.005, wt/wt) blended films were about 10⁻² M. Thus, the incident light does not completely reach the bottom of the samples with greater than 5000 molar absorption coefficient values. However, photocuring was accomplished due to dark reaction derived from the living nature of the generated active species such as the oxonium cation.

A photo-DSC thermogram of the 200-μm-thick ERL-4221/DPTPSP (1:0.005, wt/wt) blended film upon irradiation at 300 nm in N₂ is shown in Fig. 3. The heat generation started, reached a maximum value, then decreased with the irradiation time. The conversion was calculated using the sum of the heat [24]. Based on the photo-DSC measurements, the conversion was not proportional to the irradiation dose. Figure 4 shows the photo-DSC thermograms of the 200-μm-thick ERL-4221/PAGs (1:0.005, wt/wt) blended film upon irradiation at 285 nm. The effect of the structures of the PAGs was clearly observed. Table 1 summarizes the maximum values of the heat and irradiation time when the maximum value of the heat was observed. In addition, the conversion values after irradiation for 1200 seconds also are summarized in Table 1. In order to discuss the structure-property relationships, the molar absorption coefficient values of the PAGs are also summarized in Table 1.

![Figure 3](image3.png)

**Fig. 3.** Photo-DSC curves of 200-μm-thick ERL-4221/DPTPSP (1:0.005, wt/wt) blended film upon irradiation at 300 nm in N₂. Solid line: heat flow. Broken line: conversion. Light intensity: 0.70 mW/cm².

![Figure 4](image4.png)

**Fig. 4.** Photo-DSC curves of 200-μm-thick ERL-4221/PAG (1:0.005, wt/wt) blended film upon irradiation at 285 nm in N₂. Solid line: TTSP, dotted line: DPTPSP, broken line: THIP, bold line: DIP. Light intensity: 0.74 mW/cm².
The photocuring efficiencies were in the order, TTSP > DPTPSP > THIP > DIP upon irradiation at 254 nm and there is no relationship between the photocuring efficiency and molar absorption coefficients of the PAGs. This phenomenon may be due to the strong absorption effect of the incident light at that wavelength. The low efficiency of the DIP at any investigated wavelength is due to the low reactivity of the iodonium salts compared to those of the sulfonium salts.

Upon irradiation at 285 nm, the efficiencies were in the order, DPTPSP > TTSP > THIP > DIP. The highest efficiency using DPTPSP is due to the high absorption ($\epsilon$ value at 285 nm: 12380). The relatively low efficiency using THIP may be due to the basic property of the imide ring in the THIP.

When the irradiations were performed at 300 nm, the efficiencies were in the order, DPTPSP > THIP > TTSP = DIP. The highest efficiency using DPTPSP is due to the high absorption ($\epsilon$ value at 300 nm: 17350). The relatively low efficiency using TTSP is due to its low absorption.

We developed THIP as an i-line sensitive PAG [23]. Thus, the photocuring efficiency of THIP was the highest among the PAGs investigated upon irradiation at 365 nm.

The strong interest is to compare the efficiency using deep UV LEDs or conventional light sources such as a medium pressure mercury lamp. There are many line spectra in the emission of the medium mercury lamp. To compare the efficiencies, the power of the irradiation light from the medium pressure mercury lamp was adjusted to 0.74 mW/cm$^2$ in the range of 200 to 400 nm, the same value as the 285-nm emission from the deep-UV LED.

Upon irradiation using the medium pressure mercury lamp, the efficiencies were in the order, DPTPSP > THIP > TTSP > DIP. The irradiation light contained a 30% intensity at 365 nm. Thus, the highest efficiency using DPTPSP is mainly due to the high absorption at less than 313-nm light. We concluded that DPTPSP had the highest efficiency among the PAGs regardless of the investigated wavelength.

| PAG   | irradiation wavelength (nm) | irradiation intensity (mW cm$^{-2}$) | $\epsilon \times 10^4$ (L mol$^{-1}$ cm$^{-1}$) | maximum heat flow (W g$^{-1}$) | time at maximum heat flow (min) | conversion after irradiation for 1200 s (%) |
|-------|---------------------------|-----------------------------------|---------------------------------|--------------------------------|-------------------------------|----------------------------------------|
| TTSP  | 254                       | 0.28                              | 2.000                           | 0.41                           | 0.39                          | 10.4                                   |
| DIP   | 254                       | 0.28                              | 1.059                           | 0.00                           | -                             | 0.0                                    |
| DPTPSP| 254                       | 0.28                              | 0.743                           | 0.19                           | 0.60                          | 8.1                                    |
| THIP  | 254                       | 0.28                              | 2.147                           | 0.09                           | 0.92                          | 3.7                                    |
| TTSP  | 285                       | 0.74                              | 0.036                           | 0.19                           | 1.44                          | 11.4                                   |
| DIP   | 285                       | 0.74                              | 0.189                           | 0.00                           | -                             | 0.0                                    |
| DPTPSP| 285                       | 0.74                              | 1.238                           | 0.31                           | 0.39                          | 10.8                                   |
| THIP  | 285                       | 0.74                              | 0.842                           | 0.19                           | 0.82                          | 6.0                                    |
| TTSP  | 300                       | 0.70                              | 0.003                           | 0.00                           | -                             | 0.0                                    |
| DIP   | 300                       | 0.70                              | 0.051                           | 0.00                           | -                             | 0.0                                    |
| DPTPSP| 300                       | 0.70                              | 1.735                           | 0.45                           | 0.36                          | 14.5                                   |
| THIP  | 300                       | 0.70                              | 0.619                           | 0.26                           | 0.78                          | 7.0                                    |
| TTSP  | 365                       | 2.00                              | 0.000                           | 0.00                           | -                             | 0.0                                    |
| DIP   | 365                       | 2.00                              | 0.000                           | 0.00                           | -                             | 0.0                                    |
| DPTPSP| 365                       | 2.00                              | 0.005                           | 1.22                           | 0.56                          | 23.2                                   |
| THIP  | 365                       | 2.00                              | 0.275                           | 2.12                           | 0.41                          | 23.7                                   |
| TTSP  | no filter$^a$             | 0.74$^b$                          | -                               | 0.18                           | 0.54                          | 8.4                                    |
| DIP   | no filter$^a$             | 0.74$^b$                          | -                               | 0.08                           | 2.89                          | 7.0                                    |
| DPTPSP| no filter$^a$             | 0.74$^b$                          | -                               | 0.70                           | 0.34                          | 21.0                                   |
| THIP  | no filter$^a$             | 0.74$^b$                          | -                               | 0.37                           | 0.67                          | 15.9                                   |

$^a$ Medium pressure mercury lamp was used as the light source. $^b$ Accumulated light intensity between 200 and 400 nm. $^c$ Peak maximum was not observed.
wavelengths except at 254 nm.

Photocuring on a Si wafer was carried out using deep-UV LEDs to investigate the photocuring efficiency of thin films. The mixture of the ERL-4221 epoxy monomer and PAGs was coated and adjusted to 13 µm due to technical limitations. Conversion of the epoxy unit in the ERL-4221 was monitored by FT-IR spectroscopy. Figure 5 shows the FT-IR spectral changes of the 13-µm-thick ERL-4221/DPTPSP (1:0.005, wt/wt) blended film upon irradiation at 285 nm in air. The conversions of the epoxy groups in the film were determined by the decrease in the peak at 970 cm\(^{-1}\) in the FT-IR spectra. After irradiation for 20 min, a 50% decrease in the peak was observed.

![FT-IR spectral changes](image)

**Fig. 5.** FT-IR spectral changes of 13-µm-thick ERL-4221/DPTPSP (1:0.005, wt/wt) blended film upon irradiation at 285 nm in air. Bold line: before irradiation. Solid line: after irradiation. Irradiation time: 20 min. Light intensity: 0.74 mW/cm\(^2\).

The effects of the irradiation dose and irradiation wavelength on the conversion were investigated using DPTPSP as a PAG. Figure 6 shows the effect of the irradiation dose on the conversion of the 13-µm-thick ERL-4221/DPTPSP (1:0.005, wt/wt) blended film upon irradiation in air. The conversion proportionally increased with the irradiation dose during the initial stage (conversion: <30%) regardless of the irradiation wavelengths. Photocuring efficiencies were in the order, 300-nm light > 285-nm light > 265-nm light and the light from the medium pressure mercury lamp > 365-nm light. The lowest photocuring efficiency using the 365-nm light is due to the low absorption of the incident light in the experimental film thickness (13 µm). The relatively low photocuring efficiency using the medium pressure mercury lamp is accountable by considering that the 30% amount of the irradiation dose in the medium pressure mercury lamp is ascribed as the 365-nm light.

![Conversion vs. Irradiation dose](image)

**Fig. 6.** Conversion of 13-µm-thick ERL-4221/DPTPSP (1:0.005, wt/wt) blended films upon irradiation at 265 nm (□), 285 nm (△), 300 nm (○), and 365 nm (●) in air. For comparison, conversion of 13-µm-thick ERL-4221/DPTPSP (1:0.005, wt/wt) blended films upon irradiation using medium pressure mercury lamp (▲) in air is also shown.

The effects of on the irradiation wavelength and the PAGs on the photocuring efficiencies were summarized in Fig. 7. DPTPSP is the best investigated PAG regardless of the irradiation wavelengths except for 365 nm. It is noteworthy that the irradiation at 265 nm is effective for all PAGs used because of the penetration of light using the thin samples.

![Conversion vs. Irradiation wavelength](image)

The photocuring efficiencies were strongly affected by the thickness of samples, as same as those using photoradical initiators [22]. Figure 8 shows the effect of the film thickness on the conversion of ERL-4221/DPTPSP (1:0.005, wt/wt) blended film on irradiation in air.
Fig. 7. Conversion rate of 13-μm-thick ERL-4221/PAG (1:0.005, wt/wt) blended films in air.

Fig. 8. Conversion of ERL-4221/DPTPSP (1:0.005, wt/wt) blended films upon irradiation at 285 nm in air. Film thickness: 1 μm (□), 3 μm (△), 13 μm (○). For comparison, conversion of 200-μm-thick ERL-4221/DPTPSP (1:0.005, wt/wt) blended films upon irradiation at 285 nm in air obtained from a Photo-DSC measurement is also shown in the black line.

The photocuring efficiency using DPTPSP was in the order, 3 μm-thick film > 13 μm-thick film > 1 μm-thick film > 200 μm-thick film. The decreased photocuring efficiency of the 1 μm-thick film is due to inhibition from water vapor in the atmosphere, and the decreased efficiencies of the 13 or 200 μm-thick films are derived from the decreased light penetration.

The effect of the film thickness on the photocuring efficiency upon irradiation at 265 nm was also investigated using other PAGs (Fig. 9).

Fig. 9. Conversion of ERL-4221/ PAG (1:0.005, wt/wt) blended films upon irradiation at 265 nm in air. PAG: (a) DIP, (b) TTSP, (c) DPTPSP. Film thickness: 1 μm (□), 3 μm (△), 13 μm (○).

The photocuring behaviors using TTSP were not affected by the film thickness below 13 μm upon irradiation at 265 nm. Using DIP and DPTPST as PAGs, the photocuring efficiencies increased with the film thickness up to 13 μm.
due to inhibition from water vapor in the atmosphere. Thus, we concluded that TTSP is the best PAG for irradiation at 265 nm.

Based on the discussion, light penetration is essential for a high performance photocuring system. We calculated the transmittance of the films using the experimental conditions. Table 2 summarizes the light absorption of the films containing the ERL-4221 monomer and PAGs. It is desirable to use conditions which show a 10% transmittance. Thus, we concluded that less than a 100-μm thick film is desired to obtain high photocuring efficiencies.

Table 2. Film thickness of ERL-4221/PAG (1:0.005, wt/wt) blended films which show a 10% transmittance.

| Wavelength (nm) | Film thickness (μm) |
|-----------------|---------------------|
|                 | DIP | TTSP | DPTPSP | THIP |
| 254             | 60  | 32   | 76     | 38   |
| 265             | 111 | 62   | 92     | 56   |
| 285             | 315 | 663  | 64     | 103  |
| 300             | 854 | 1570 | 47     | 144  |
| 365             | 6547| 8743 | 6313   | 342  |

4. Conclusion

We investigated the formulations of epoxy resins which were applicable for deep UV LED lamps. The mixtures of the ERL-4221 epoxy monomer and PAGs were placed on aluminum pans or silicon wafers to obtain sample films. The films were irradiated by deep UV LEDs which emit 265, 285 or 300-nm light. The effects of the PAGs, irradiation wavelength, and sample thickness on the conversion of the epoxy unit was investigated using Photo-DSC and FT-IR spectroscopy. We found that the PAG diphenyl[(4-phenylthio)phenyl]sulfonium hexafluorophosphate (DPTPSP) was the most effective PAG investigated for irradiation at 285 and 300 nm due to its strong absorption at these wavelengths. Upon irradiation at 265 nm, TTSP was the most effective PAG to suppress the inhibition of water vapor from the atmosphere for less than 13-μm thick films. We also found that less than 100-μm thick films could be effectively cured upon irradiation by the deep-UV LEDs.

References
1. J. P. Fouassier and J. F. Rabek, “Radiation Curing in Polymer Science and Technology”, Elsevier Applied Science, New York (1993).
2. B. A. Ficek, A. M. Thiesen, and A. B. Scranton, Eur. Polym. J., 44 (2008) 98.
3. M. Flores, A. M. Tomuta, X. Fernandez-Francos, X. Ramis, M. Sangermano, and A. Serra, Polymer, 54 (2013) 5473.
4. M. Barletta, S. Vesco, M. Puopolo, and V. Tagliaferri, Surf. Coat. Technol., 272 (2015) 322.
5. M. Sangermano, G. Buzzero, R. Rizzoli, L. Ortolani, V. Morandi, F. Pirri, and A. Chiolerio, Macromol. Chem. Phys., 216 (2015) 707.
6. D. K. Basker, M. A. Brook, and K. Saravanamuttu, J. Phys. Chem. C, 119 (2015) 20606.
7. S. Nagai, K. Yamada, A. Hirano, M. Ippomatsu, M. Ito, N. Morishima, K. Aosaki, Y. Honda, H. Amano, and I. Akasaki, Jpn. J. Appl. Phys., 55 (2016) 082101.
8. J. H. Park, J. W. Lee, D. Y. Kim, J. Cho, E. F. Schubert, J. Kim, J. Lee, Y.-I. Kim, Y. Park, and J. K. Kim, J. Appl. Phys., 119 (2016) 023101.
9. W. Guo, F. Xu, Y. Sun, L. Lu, Z. Qin, T. Yu, X. Wang, and B. Shen, Superlatt. Microstruct., 100 (2016) 941.
10. J.-Y. Bae, H.-Y. Kim, Y.-W. Lim, Y.-H. Kim, and B.-S. Bae, RSC Adv., 6 (2016) 26826.
11. M. Valledor, J. C. Campo, F. J. Ferrero, E. Sotelo, M. T. Fernández-Argüelles, J. M. Costa-Fernandez, and A. Sanz-Medel, Sens. Actuat. B: Chem., 233 (2016) 574.
12. K. Yamada, Y. Furusawa, S. Nagai, A. Hirano, M. Ippomatsu, K. Aosaki, N. Morishima, H. Amano, and I. Akasaki, Appl. Phys. Express, 12 (2015) 012101.
13. H. Okamura, S. Niiziike, T. Ouchi, and A. Matsumoto, J. Photopolym. Sci. Technol., 29 (2016) 99.
14. J. V. Crivello, J. Polym. Sci. Part A: Polym. Chem., 37 (1999) 4241.
15. M. Shirai and M. Tsunooka, Prog. Polym. Sci., 21 (1996) 1.
16. H. Okamura and M. Shirai, Trends Photochem. Photobiol., 15 (2013) 51.
17. S. Shi, X. Allonas, C. Croute-Barghorn, and A. Chemtob, New J. Chem., 39 (2015) 5686.
18. P. Xiao, F. Dumur, B. Graff, F. Morlet-Savary, D. Gigmes, J. P. Fouassier, and J. Lalevée, *Macromolecules*, **47** (2014) 973.
19. J. Zhang, P. Xiao, C. Dietlin, D. Campolo, F. Dumur, F. Morlet-Savary, D. Gigmes, F. Morlet-Savary, J. P. Fouassier, and J. Lalevée, *Macromol. Chem. Phys.*, **217** (2016) 1214.
20. J. V. Crivello and M. Jang, *J. Photochem. Photobiol. A: Chem.*, **159** (2003) 173.
21. M.-A. Tehfe, F. Dumur, P. Xiao, J. Zhang, B. Graff, F. Morlet-Savary, D. Gigmes, J.-P. Fouassier, and J. Lalevée, *Polymer*, **55** (2014) 2285.
22. S. I. Hong, T. Kurosaki, and M. Okawara, *J. Polym. Sci. Polym. Chem. Ed.*, **12** (1974) 2553.
23. H. Okamura, H. Naito, and M. Shirai, *J. Photopolym. Sci. Technol.*, **22** (2009) 583.
24. B. Golaz, V. Michaud, Y. Leterrier, and J.-A. E. Månson, *Polymer*, **53** (2012) 2038.