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Moisture-resistant and highly adhesive acrylate-based sealing materials embedded with oxime-based photoinitiators for hermetic optical devices

Seung-Rak Son, Jongil An, Jin-Wook Choi, Soyern Kim, Jisung Park, Chan Beom Park, and Jun Hyup Lee†

Department of Chemical Engineering, Soongsil University, Seoul 06978, Korea

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Abstract−The hermetic sealing of optoelectronic devices has attracted much attention because it can endow the devices with long-term operation reliability and high mechanical resistance. Herein, we present a facile and efficacious strategy for fabrication of water-resistant and highly adhesive acrylate-based sealing materials for hermetic optical devices using oxime-based photoinitiators. Compared with conventional sealing materials containing ketone-based photoinitiator, those embedded with oxime-based photointiators afforded a strong UV absorption in the effective wavelength range, a high UV curing conversion of 99.5% at a low radiant energy of 1.0 J cm^{-2}, a remarkable adhesion strength of 42.2 kgf cm^{-2}, an improved water impermeability of 5.3 g m^{-2} day^{-1}, and a reduced internal pollution length of 104.9 μm. These excellent properties of the fabricated sealing materials are attributed to the fragmentation mechanism of oxime-based photoinitiators which can generate numerous initiating radicals through multi-step decomposition reactions, resulting in the efficient initiation for photoreaction with acrylate resins. This study provides promising sealing materials based on the oxime-based photoinitiators for ultra-slim and flexible optoelectronic applications.

Keywords: Acrylate Resin, Hermetic Sealing, Optoelectronic Device, Photoinitiator, UV Curing

INTRODUCTION

The display industry has been demonstrating an increasing demand for advanced display devices such as ultra-slim displays, foldable devices, and tilted displays. In general, liquid crystal (LC) modes have several advantages, such as high picture quality and low power consumption, and are used in various display devices requiring super narrow bezel, flexibility, and scalability characteristics [1-6]. However, in order to apply LCs to the above-mentioned display devices, the electronic adhesives for hermetic devices should ensure not only superior physical properties, such as high adhesion strength, low water permeability, and low internal contamination of LCs, but also fast and stable UV curing characteristics.

Conventional electronic adhesives for displays are commonly composed of appropriate amounts of acrylate resins, epoxy resins, photoinitiator, thermal curing agent, and inorganic or organic fillers [7-10]. Among them, the acrylate resin as a major component and photoinitiator is firmly cured by free radical polymerization through a UV-triggered photoinitiation, and therefore results in the formation of interpenetrating polymer network (IPN) structure [11-16]. This photocuring system has several advantages, such as low energy consumption, low environmental pollution, low curing shrinkage, high chemical stability, structural stability, and very rapid curing rate at ambient temperature [17-19]. Therefore, photocuring systems are often used in the assembly of various electronic devices for achieving the objectives of adhesion, encapsulation, and protection, as well as in painting, inking, and coating [20-25].

When common acrylate-based electronic adhesives are cured through a UV photoreaction, the photoinitiator in the adhesives readily decomposes to generate free radicals or reactive ions, and initiates the photocuring reaction, thereby rendering the acrylate monomers to be cross-linked through a continuous reaction [26]. To increase the initiation efficiency for UV curing, the proper selection of a highly reactive photoinitiator is quite essential. An ideal photoinitiator should have excellent optical absorbance in the active region, high quantum efficiency for radical formation, high solubility for the monomer, no yellowing, long-term storage stability, and price competitiveness [27]. However, to the best of our knowledge, there have been no studies that have examined the relationship between the structure of photoinitiator and performance of acrylate-based electronic adhesives for hermetic LC devices.

In this work, we have fabricated high-performance acrylate-based sealing materials embedded with oxime-based photoinitiators that simultaneously ensure high adhesion strength and excellent moisture-tolerance for hermetic LC displays. To investigate the effect of the structure of photoinitiator on the performance of optoelectronic adhesives, four types of photoinitiators were employed to prepare acrylate-based sealing materials, as shown in Fig. 1. The ketone-based photoinitiator of Irgacure 651 is commonly utilized for commercial LC devices and was used as a reference material. To identify the effect of long-wavelength absorption and bulky chemical structure on the performance of sealing materials, the titanocene-based photoinitiator of Irgacure 784 was applied to adhesive system. Furthermore, to understand the efficient fragmentation mechanism of photoinitiator, oxime-based photoinitiators of Irgacure OXE 01 and 02 were embedded in acrylate-based sealing materials. The UV and visible absorbances, UV curing conversion, adhesive strength, water permeability, and LC contamination level were examined

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†To whom correspondence should be addressed.
E-mail: junhyuplee@ssu.ac.kr

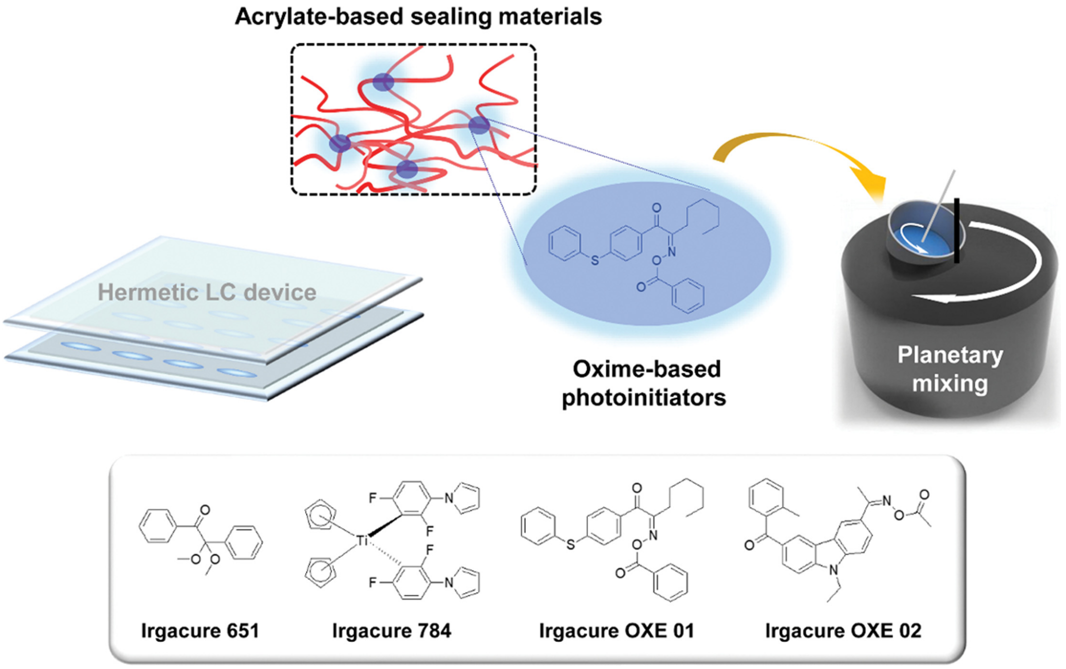


Fig. 1. Schematic illustration of high-performance acrylate-based sealing materials containing different types of photoinitiators.

for the newly prepared acrylate-based sealing materials containing the different types of photoinitiators.

EXPERIMENTAL

1. Materials

The acrylate resin used in the sealing materials was bisphenol A glycerolate dimethacrylate (BisGMA, Sigma-Aldrich Korea, Seoul, Korea). The epoxy resin was a bisphenol A type epoxy resin (YD-128, Kukdo chemical, Seoul, Korea). The thermal curing agent for curing of epoxy resin was adipic acid dihydrazide (ADH, Sigma-Aldrich Korea, Seoul, Korea). The fumed silica particle with an average size of 250 nm (Sigma-Aldrich Korea, Seoul, Korea) was used as inorganic filler. The photoinitiators presented in Fig. 1 are 2,2-dimethoxy-1,2-diphenylethan-1-one (Irgacure 651, BASF, Ludwigshafen, Germany), bis(.eta.5-2,4-cylcopentadien-1-yl)-bis(2,6-difluoro-3-(1H-pyrrol-1-yl)-phenyl) titanium (Irgacure 784, BASF, Ludwigshafen, Germany), [1-(4-phenylsulfanylbenzoyl)heptylideneamino]benzoate (Irgacure OXE 01, BASF, Ludwigshafen, Germany), and [1-[9-ethyl-6-(2-methylbenzoyl)carbazol-3-yl]ethylideneamino] acetate (Irgacure OXE 02, BASF, Ludwigshafen, Germany).

2. Preparation of Acrylate-based Sealing Materials

High-performance acrylate-based sealing materials containing different types of photoinitiators were fabricated by mixing an acrylate resin of BisGMA (64.0 g), an epoxy resin of YD-128 (16.0 g), a hardener of ADH (1.5 g), an inorganic silica filler (16.0 g), and a photoinitiator (2.5 g). These constituents were homogeneously blended using a revolution/rotation-type planetary mixer (AR-100, Thinky, Tokyo, Japan). The mixing process was performed for 30 min at a revolution/rotation speed of 2,000/800 rpm before being defoamed for 5 min at 2,200/0 rpm, leading to the viscous adhesive products.

3. Characterization

To measure the UV and visible absorbance of the photoinitiators, we dissolved photoinitiators of 1 wt% in acetonitrile and measured the absorbance spectrum with a UV-visible (UV-vis) spectrophotometer (S-3100, Scinco, Seoul, Korea). For the measurements, a quartz cell with a path length of 1 cm was used, and the wavelength band was set between 200 and 800 nm. The UV curing rate of the sealing materials was measured by Fourier transform infrared spectroscopy (FT-IR, FT/IR-460 Plus, Jasco, Easton, PA, USA) before and after UV photoreaction; the FT-IR spectrometer was equipped with an attenuated total reflectance (ATR) accessory. The UV curing rate was calculated by comparing the peak areas of the acrylate group before and after curing of the prepared sealing materials.

To evaluate the adhesive strength of the prepared sealing materials, the viscous products were painted in a 3 mm diameter between two crossed sheets of indium tin oxide (ITO) glass. The prepared ITO assembly was hardened under 365 nm UV irradiation with a radiant energy of 3.0 J cm^{-2} (WUV-L50, Daihan Labtech, Seoul, Korea), and then was annealed for 60 min at 120 °C. The adhesive strength was measured using a universal testing machine (UTM, LR-5K, Lloyd, Bognor Regis, UK) at 25 °C with a crosshead speed of 1.3 mm min^{-1} according to ASTM C663 standard.

To assess the water permeability of the sealing materials, we used an ITO glass and a glass bottle with a 3 cm opening at the top. We first placed 0.5 g of drierite (W. A. Hammond Drierite Co., Ltd, Xenia, OH, USA) as a moisture absorbent in the glass bottle, and then painted the sealing materials evenly onto the top surface of the bottle. Finally, the ITO glass was placed on top of the bottle and allowed to be cured under the same curing conditions for the measurement of adhesive strength. The assembly of ITO glass and bottle was immersed in water at 60 °C for 2 h and then the weight of the drierite was measured, to calculate the water permeability of sealing materials.

The LC contamination level was estimated using nematic LC of fluorobiphenyl compound with alkyl groups (T_{NI}=75 °C, Δn=0.095, $\Delta\varepsilon$=−3.1, Merck) and ITO substrate coated with a polyimide (PI, AL607XX, JSR, Tokyo, Japan). The ITO glass substrate was coated with a PI layer using a spin coater before being baked on a hotplate at 80 °C for 10 min, followed by baking in an oven at 230 °C for 1 h. The prepared sealing materials were placed between the two PI-coated ITO substrates and cured under the same curing conditions for adhesive strength measurements, and then the LC was injected into the ITO cell through a capillary action. To confirm the contamination level of internal LC materials, the optical texture of LCs near the sealing materials was inspected using a polarized optical microscope (POM, BX51, Olympus, Tokyo, Japan).

RESULTS AND DISCUSSION

In this study, we prepared water-resistant and highly adhesive electronic sealing materials using a bisphenol A type acrylate resin as a main component together with epoxy resin, heat curing agent, silica filler, and photoinitiators. In addition, various types of photoinitiators were employed to sealing materials, and their effect on the performance of sealing materials including UV curing conversion, adhesion strength, water permeability, and LC contamination level were investigated. As shown in Fig. 2, we first identified the UV-vis absorbance of the different types of photoinitiators. We measured the solution of 1 wt% photoinitiator in acetonitrile using a UV-vis spectrophotometer and examined the absorption dependency on the structure of photoinitiator. Usually, the effective UV wavelength range used for industrial photo-curing process of electronic adhesives is from 300 to 400 nm. In the case of the ketone-based Irgacure 651, peaks at wavelengths less than 300 nm show extremely large absorbances; however, a broad band between 300 and 400 nm is relatively weak and are, thus, hardly observed, indicating the low initiation efficiency for curing of sealing materials. However, the titanocene-based Irgacure 784 is not only UV-active in the wavelength range between 200 and 400 nm, but also shows a long absorption tail up to visible light region of 500 nm. Compared with other sealing materials containing Irgacure 651, OXE 01, and OXE 02, titanocene-based adhesive showed a different red color due to the blue light absorption (Fig. 2). This visible light absorption may reduce the long-term storage stability of Irgacure 784 due to the potential exposure to external visible light. In case of oxime-based photoinitiators (Irgacure OXE 01 and 02), a strong UV absorption peak was detected in the range of 300 to 400 nm owing to the presence of a few aromatic rings, indicating the high photoinitiation efficiency in the industrial UV curing process for electronic sealing materials.

From Fig. 3, we confirmed the degree of photo-curing for the prepared sealing materials containing the different types of photoinitiators after UV treatment. The change in the C=C double bond peak before and after UV irradiation was investigated by identifying the peak area at 1,636 cm^{-1}, and UV curing conversion was obtained by varying the UV exposure energy on the sealing materials. The UV conversion ratio was calculated by Eq. (1).

$$\text{UV curing ratio (\%)} = \frac{\text{Area}_{pure} - \text{Area}_{cured}}{\text{Area}_{pure}} \times 100 \qquad (1)$$

where Area_{pure} and Area_{cured} denote the peak area of carbon-carbon double bond before and after UV treatment, respectively. Fig. 3(a) shows that the intensity of C=C double bond peaks for all sealing materials decreased after UV treatment with an energy of 1.0 J cm^{-2}, suggesting that the bisphenol A type acrylate resin is readily photopolymerized by the initiation reaction of the photoinitiators. Quantitative analysis on the change in the peak area of C=C double bond before and after UV treatment was carried out to compare the photoreaction efficiencies of the different types of photoinitiators in the prepared acrylate-based sealing materials. Fig. 3(b) shows that the UV curing conversion of sealing material with con-

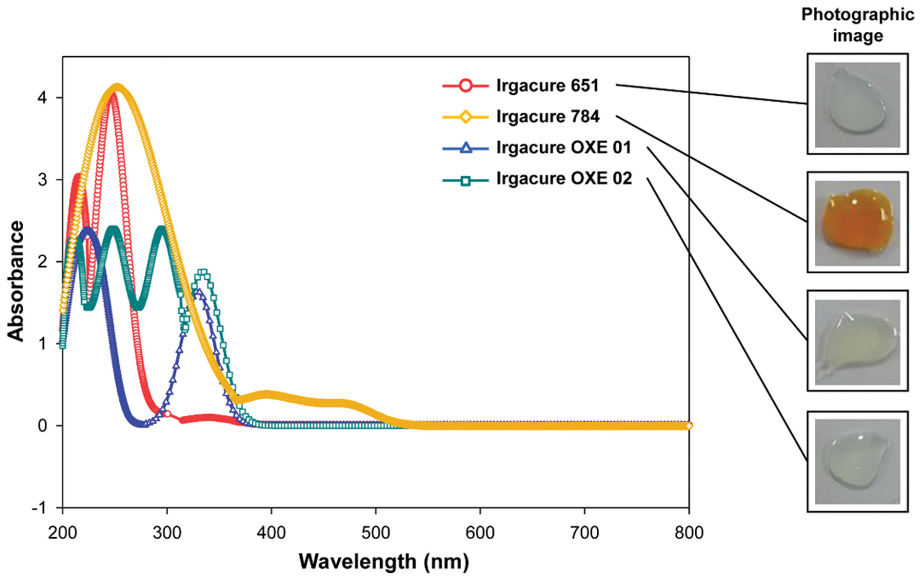


Fig. 2. UV-vis absorption spectra of various types of photoinitiators and the photographic images of the fabricated sealing materials.

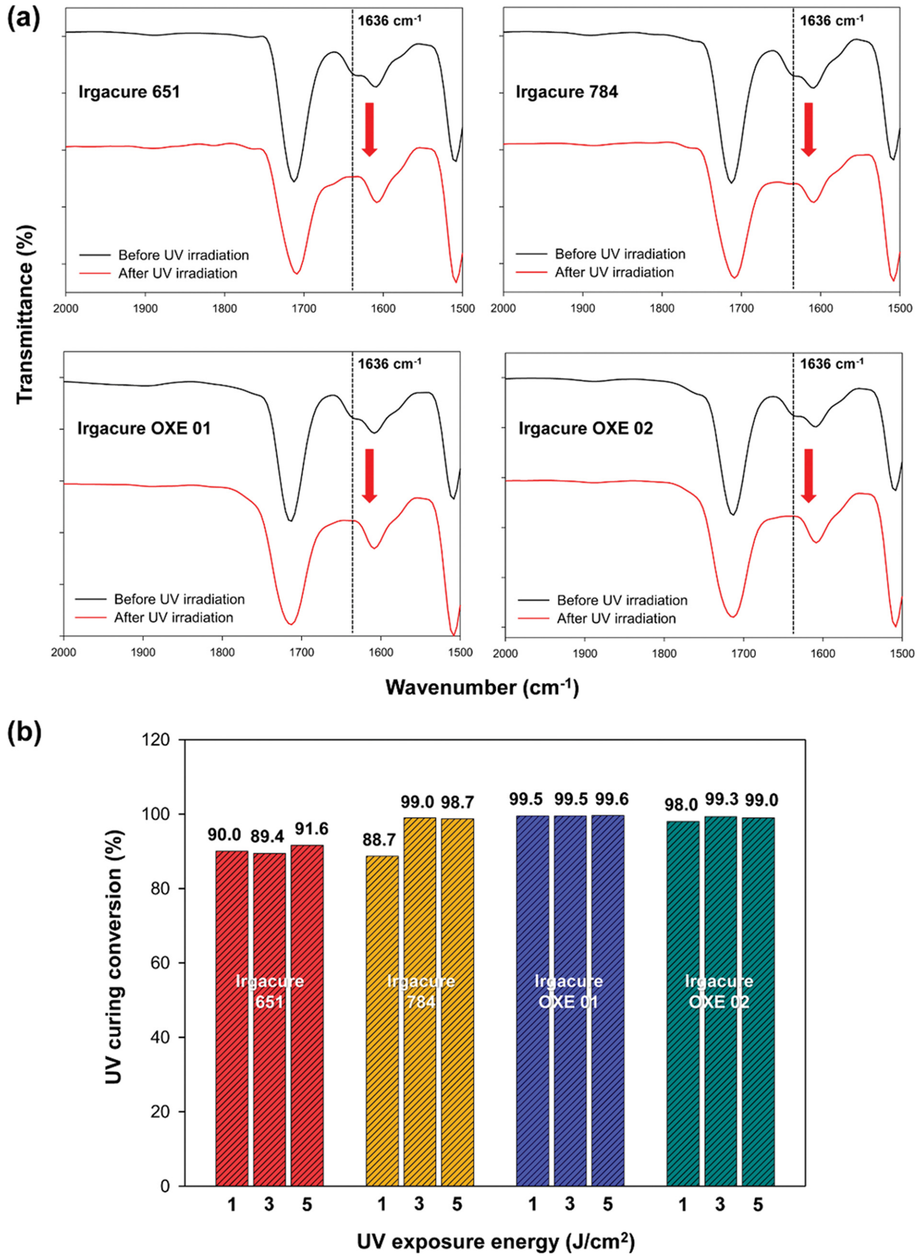


Fig. 3. (a) FT-IR spectra of the prepared sealing materials with the different types of photoinitiators before and after UV treatment with an energy of 1.0 J cm^{-2}. (b) UV curing rates of the prepared sealing materials with various types of photoinitiators according to the UV exposure energy.

ventional ketone-based Irgacure 651 is approximately 91% even when the UV exposure energy is increased from 1 to 5 J cm^{-2}. As mentioned, the UV absorbance of Irgacure 651 in the effective wavelength range of 300 to 400 nm is relatively low, resulting in the low initiation efficiency for photopolymerization of acrylate resins. In the case of titanocene-based Irgacure 784, relatively high UV curing conversion of approximately 99% was observed as the UV exposure energy increased to 3 J cm^{-2} or more. The increased UV absorbance of Irgacure 784 in the range of 300 to 400 nm leads to the improved photoinitiation for acrylate resins compared to that of Irgacure 651. In case of oxime-based Irgacure OXE 01 and 02, extremely high UV curing conversion of approximately 99% was obtained even after low-energy UV treatment of 1.0 J cm^{-2}, which is attributed to the high absorbance performance between the UV wavelengths of 300 and 400 nm. As a consequence, highly efficient and fast-curing acrylate-based sealing materials can be fabricated by using oxime-based photoinitiators.

To examine the adhesive properties of the prepared sealing materials containing the different types of photoinitiators, the adhesion strength was measured using a UTM according to ASTM C663 standard. As shown in Fig. 4, the adhesion evaluation was conducted on the test specimens of sealing materials painted between two ITO substrates, and the average value of five measurements for each specimen was obtained for adhesive strength. From Fig.

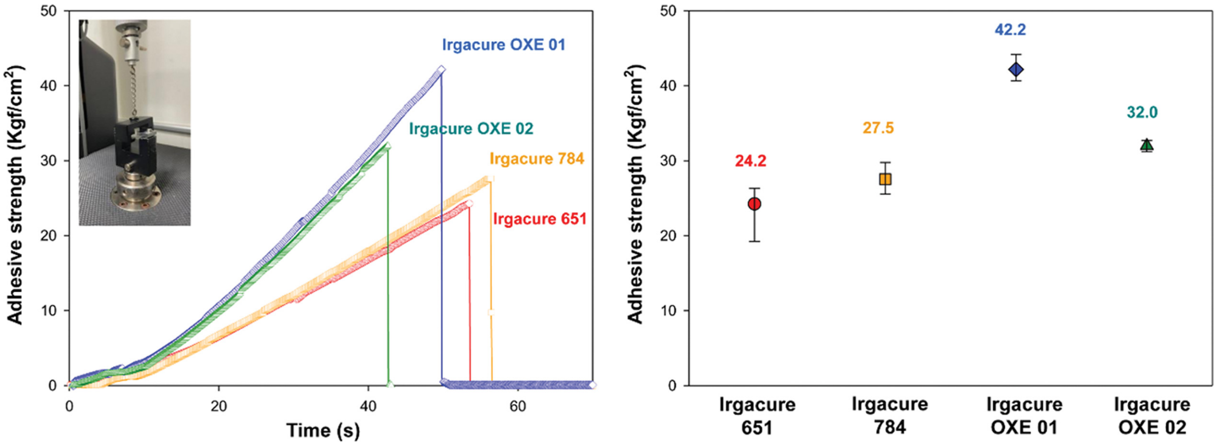


Fig. 4. Adhesive strengths of the prepared sealing materials containing different types of photoinitiators.

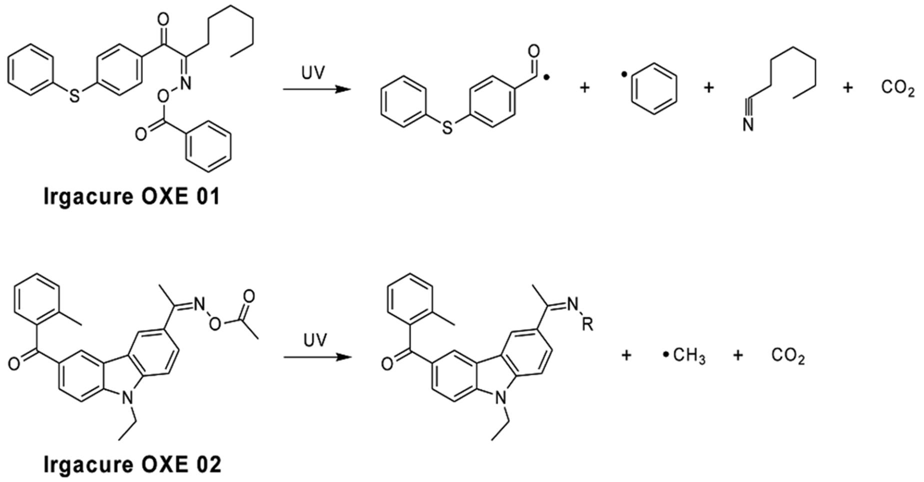


Fig. 5. Fragmentation mechanism of oxime-based photoinitiators.

4, the adhesive strengths of the sealing materials containing Irgacure 651 and Irgacure 784 are measured as 24.2 and 27.5 kgf cm^{-2}, respectively, and those of the electronic adhesives embedded with Irgacure OXE 01 and 02 are recorded as 42.2 and 32.0 kgf cm^{-2}, respectively. The former two sealing materials have relatively low adhesion strengths owing to the low curing efficiency in the effective wavelength range of 300 to 400 nm. Moreover, the titanocene-based Irgacure 784 commonly yields a bulky titanium-centered diradical during UV irradiation, resulting in the inefficient migration of the initiating species within the resin matrix, which could reduce the adhesion property of the acrylate-based sealing materials [28]. However, as the fabricated sealing materials containing oxime-based photoinitiators have relatively high curing efficiency as described above, they exhibit improved adhesion strength for hermetic LC devices. In particular, the acrylate-based sealing material with Irgacure OXE 01 shows a higher adhesion strength than that with Irgacure OXE 02, which may be attributed to the fragmentation mechanism of these oxime-based photoinitiators. As shown in Fig. 5, Irgacure OXE 01 can generate two initiating radicals through multi-step decomposition reactions, whereas only one active radical is formed from Irgacure OXE 02, which results in the more efficient initiation of oxime-based OXE 01 initiator in the photoreaction with acrylate resins [29].

To investigate the relationship between the structure of photoinitiators and moisture barrier properties of the fabricated sealing materials, water permeability evaluations were conducted for those with different types of photoinitiators. The water molecules that penetrated from external humid environment would reduce the voltage holding ratio of LC device, leading to a deterioration in the image quality of display device [30,31]. As shown in Fig. 6, the values of water permeability were measured using drierite as a moisture absorbent. The sealing materials containing Irgacure 651 and 784 exhibited relatively high water permeability of 11.9 and 9.3 g m^{-2} day^{-1}, respectively, owing to the relatively low UV absorption and inefficient migration of the bulky initiating radical. However, the oxime-based photoinitiators, including Irgacure OXE 01 and 02, which have excellent initiation efficiency for photopolymerization of acrylate resins, showed remarkably low water permeability values of 5.3 and 7.9 g m^{-2} day^{-1}, respectively. Notably, Irgacure OXE 01 exhibited the lowest water permeability of 5.3 g m^{-2} day^{-1}, which is more than two-times lower than that of conventional ketone-based Irgacure 651 (11.9 g m^{-2} day^{-1}), among the tested

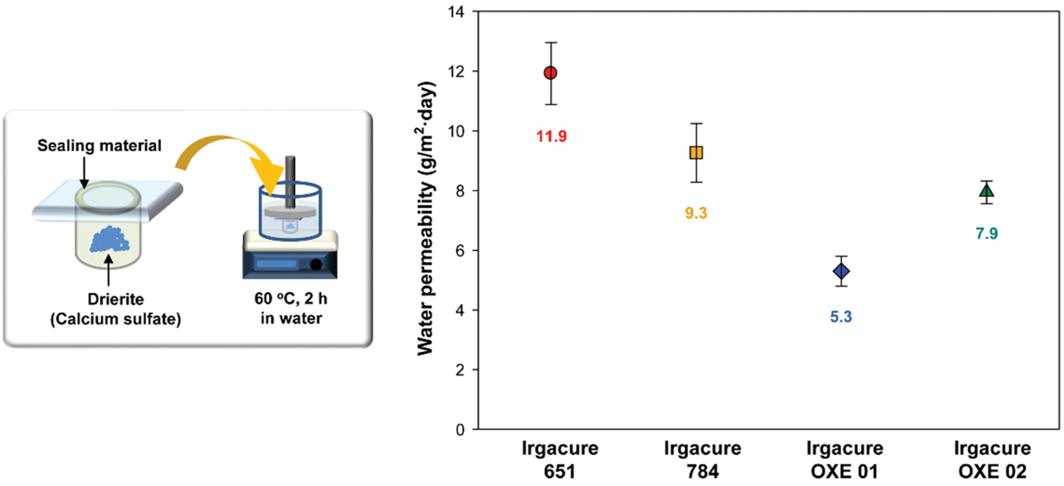
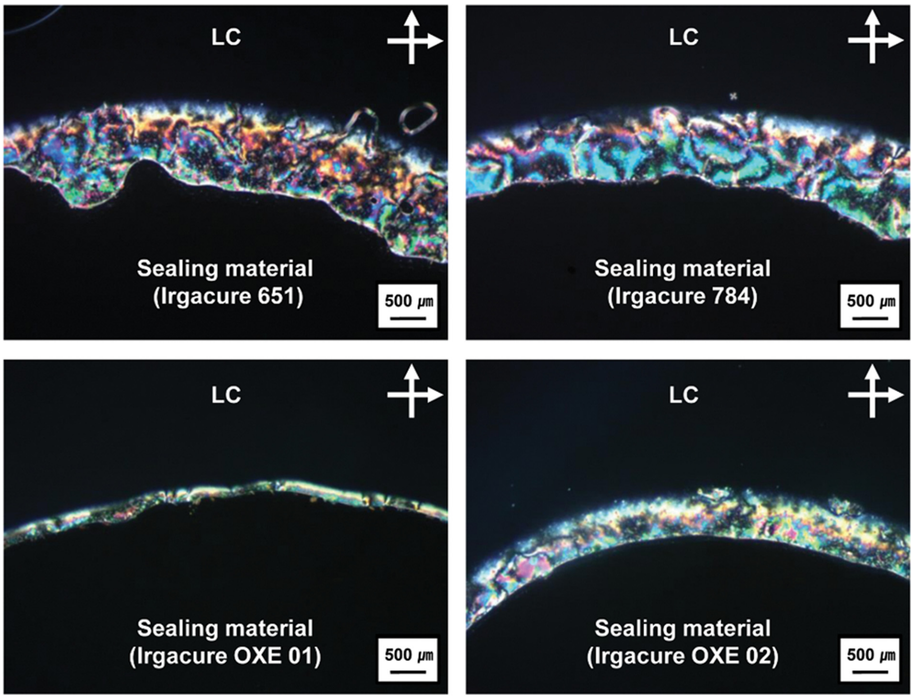


Fig. 6. Water permeabilities of the prepared sealing materials with various types of photoinitiators.



	Irgacure 651	Irgacure 784	Irgacure OXE 01	Irgacure OXE 02
LC Pollution length	1294.1 μm	946.9 μm	104.9 μm	536.7 μm

Fig. 7. POM images and LC pollution lengths of the prepared sealing materials.

photoinitiators. Since Irgacure OXE 01 provides more initiating species for photocuring of the sealing materials, a highly crosslinked network of the acrylate resins can be formed after UV irradiation, resulting in the improved water barrier performance of the sealing materials.

In the assembly process of LC devices, the sealing materials and the LCs can be in contact with each other, from the moment the LCs are injected by capillary action. After the curing process, the unreacted components of sealing materials can be eluted into the LC phase, which causes an LC defect and thereby reduces the picture quality of the LC device [32,33]. To examine the internal contamination levels of the prepared sealing materials depending on the type of the photoinitiators, the optical texture of LCs near the sealing materials was analyzed by using POM, and the mean LC pollution length for each sealing material was measured. As shown in Fig. 7, the acrylate-based sealing materials containing Irgacure

651 and Irgacure 784 showed severe disordered LC texture between sealing material and LC, and the internal contamination lengths were significantly high as 1,294.1 and 946.9 μm, respectively. Although, the sealing materials embedded with oxime-based photoinitiators exhibited extremely low LC pollution lengths of 104.9 and 536.7 μm for Irgacure OXE 01 and 02, respectively. In accordance with water permeability results, the acrylate-based sealing materials based on oxime-based photoinitiators provide excellent LC barrier property due to the high photocuring efficiency of the initiators. Particularly, sealing material with Irgacure OXE 01 offers the lowest LC contamination level, which is more than twelve-times lower than that of common ketone-based Irgacure 651, due to the formation of highly crosslinked polymer network in the sealing material.

CONCLUSIONS

High-performance acrylate-based sealing materials based on oxime-based photoinitiators were prepared to simultaneously achieve high adhesion strength, excellent moisture-tolerance, fast UV-curing rate, and low internal contamination level for hermetic LC devices. Compared with conventional ketone-based Irgacure 651, oxime-based photoinitiators, including Irgacure OXE 01 and 02, afforded strong UV absorption in the range of 300 to 400 nm, extremely high UV curing conversion even at a low UV energy of 1.0 J cm^{-2}, high adhesion strength with ITO substrates, excellent water impermeability, and reduced LC pollution length. Notably, an acrylate-based sealing material embedded with Irgacure OXE 01 exhibited the highest adhesion strength, the lowest water permeability, and the lowest LC contamination level among the fabricated sealing materials due to the formation of highly crosslinked polymer network. The proposed water-resistant and highly adhesive sealing materials based on oxime-based photoinitiators are expected to be useful for hermetic optoelectronic applications such as ultra-slim tilted displays, flexible optical devices, and tunable optoelectronic sensors.

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