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# Selective transfer of mini-light-emitting diodes via the laser-induced switching of adhesives based on azobenzene composites

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# ABSTRACT

Switchable adhesives are materials that exhibit robust bonding properties under normal conditions but, on the application of specific stimuli, exhibit easy detachability. Of particular interest is their applications in mini/micro-light-emitting diodes (LEDs). However, previous research has focused primarily on the engineering aspect of the transfer processes of these LEDs rather than on the development of switchable adhesive materials. This study presents a novel approach for the development of laser-induced switchable adhesives based on azobenzene composites by incorporating a urethane-modified azobenzene compound and a UV absorber into the adhesive. This approach results in an enhanced adhesion-switching performance and a reduction in laser-induced surface deformation. Furthermore, we investigate the relationship between the adhesion activation behavior and laser exposure conditions to identify the optimal exposure composite-based switchable adhesives have significant potential for expanding the material scope of laser-induced adhesion switching and broadening the application field of azobenzene-based switchable adhesives.

# 1. Introduction

An adhesive is a material that includes substances such as glue or cement that are utilized to bind or stick various objects together. The majority of adhesives are designed to bond strictly with the adherend for an extended period. However, there has recently been a growing demand for functional adhesives that, under certain stimuli, can detach after use. Switchable adhesives are examples of functional adhesives that possess adhesion strength comparable to that of common adhesives under standard conditions but can be easily detached under specific stimuli, such as pH [1], magnetic fields [2], solvents [3], metal ions [4], light [5–9], and heat [10–12]. The adhesion activation/deactivation process is attributed to interfacial alterations between the adherent and switchable adhesive [13] that can be instigated by several mechanisms, such as the phase transition of liquid crystals [9–12], host–guest interactions [3–5], conformational change [1], coordinate covalent bonds

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[4,7,8], crosslinking-induced hardening [14–16], and photoisomerization [5,6].

Switchable adhesives have gained popularity and are implemented in various settings. Medical tape that can be easily removed without causing any harm or irritation to the skin [15,16] and dicing tape designed for safely transporting/releasing fragile wafers [14] serve as prime illustrations of their application. One potential application area for switchable adhesives is mini/micro-light-emitting diode (LED) technologies. Mini/micro-LEDs are a novel display technology that has garnered considerable attention owing to their superior luminance and longer lifetime [17], leading to predictions of a swift expansion of their market (the compound annual growth rate of micro-LEDs between 2021 and 2027 is estimated to be 81.5 %) [18]. However, mass transfer and repair processes remain significant obstacles that will likely impact the overall cost. A method that enables fast, precise, and selective transfer is thus urgently required [19,20]. Switchable adhesives have the potential

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to meet these requirements (Fig. 1a). However, most research in this area has concentrated on the transfer methods rather than on the chemical modification of adhesive materials [21–26].

In previous studies, azobenzene-containing adhesives were studied to broaden the material scope of switchable adhesives for mini/micro-LED transfers (Fig. 1b) [27,28] or other applications [29-31]. Rapid adhesion switching was facilitated by photoisomerization of the azobenzene group, which remained consistent even after 30 activation/deactivation cycles [27,28]. In addition, selective transfer, which is a crucial step in repairing defective mini/micro-LEDs, was achieved through the selective irradiation of UV LED lamps [27]. However, a significant limitation existed in our previous research, whereby the LED lamps employed to activate azobenzene-based switchable adhesives were unsuitable for mini/micro-LEDs. Given their high power, selectivity, and rapid response, UV lasers are preferred over LED lamps for the mass transfer of mini-/micro-LEDs [21 - 26].Photoisomerization-induced adhesion switching can also be achieved by laser irradiation. However, exposure to polarized and highly intense light may induce optomechanical stress and cause surface deformation in polymer films containing azobenzene [32-34]. The formation of microscale patterns on the surface of an adhesive film can impede the attainment of conformal contact with the adherend, potentially resulting in a decreased adhesive force [35,36]. Surface deformation in azobenzene-based adhesives can be mitigated by decreasing the light intensity [32]; however, this could lead to a reduction in the switching rate. Consequently, minimizing surface deformation while maintaining a high switching rate is challenging.

In this study, novel azobenzene composite-based adhesives that enable the selective transfer of mini/micro-LEDs through laser-induced switching were developed. Furthermore, incorporating a novel azobenzene compound and UV absorber into the adhesive formulation enhanced its switching performance under laser irradiation. We also identified a relationship between the switchable adhesive activation behavior and laser power. In addition, the use of a UV absorber under optimized laser irradiation conditions effectively suppressed surface deformation. Finally, we showed that the selective transfer of mini-LEDs was successfully achieved via laser-induced switching of the prepared adhesive.

# 2. Experimental

#### 2.1. Materials

For the synthesis of azobenzene-based acrylic polymers and azobenzene compounds, the following chemicals were purchased: 4-phenylazophenol (98 %, Sigma-Aldrich), 1-chlorodecane (99 %, Sigma-Aldrich), dibutyltin dilaurate (95 %, Sigma-Aldrich), butyl acrylate (>99 %, Sigma-Aldrich), potassium carbonate (>99 %, TCI), potassium iodide (>99.5 %, TCI), 6-chloro-1-hexanol (>96 %, TCI), 1-chlorotetradecane (>98 %, TCI), hexyl isocyanate (>98 %, TCI), 2,2'-azobisisobutyronitrile (98 %, Samchun chemicals), 2-butanone (99.5 %, Samchun chemicals), N,N-dimethylformamide (99.5 %, Samchun chemicals), methanol (99.5 %, Samchun chemicals), n-hexane (96 %, Samchun chemicals), acetone (99.5 %, Samchun chemicals), ethyl acetate (99.5 %, Samchun chemicals), tetrahydrofuran (99.9 %, Samhun chemicaals), and 2-isocyanatoethyl acrylate (Showa denko). The UV absorber (2-(2hydroxy-5-methylphenyl)benzotriazole, SONGSORB® 1000) was purchased from Songwon Industrial Co. Ltd.



Fig. 1. (a) Schematic illustration of the selective transfer of mini/micro-light-emitting diodes (LEDs) via switchable adhesives. (b) Composition and switching process of azobenzene-based switchable adhesives.

A mini-LED acceptor for transfer testing was prepared by curing a dimethylpolysiloxane (PDMS) resin (SYLGARD 184, Dow Corning). A specific weight ratio of the PDMS resin and curing agent (10:0.5) was mixed using a paste mixer (ARE-310, THINKY). The mixing process consisted of two steps: mixing at 2000 rpm for 2 min and defoaming at 2000 rpm for 1 min. Subsequently, the mixture was poured into a dish and cured at 80  $^{\circ}$ C for 12 h.

#### 2.2. Preparation of azobenzene-based switchable adhesives

#### 2.2.1. Synthesis of an azobenzene-based acrylic polymer

An azobenzene-based acrylic polymer was prepared in three steps, which is described in detail in Fig. S1a. First, 6-(4-(phenyldiazenyl)) phenoxy)hexan-1-ol was synthesized using the following steps. N, N-dimethylformamide (DMF, 15 mL), 4-phenylazophenol (3.568 g, 0.018 mol), and potassium carbonate (2.488 g, 0.018 mol) were mixed for 30 min under ambient conditions. Subsequently, 6-chloro-1-hexanol (3.689 g, 0.027 mol) and potassium iodide (7.5 mg, 0.045 mmol) were added to the mixture, and the mixture was heated for reaction (110 °C, >24 h). Then, the product was precipitated using cold water and refined via recrystallization in n-hexane. The desired product was obtained via filtration and vacuum drying.

The synthesized compounds were functionalized with acrylate groups. 6-(4-(Phenyldiazenyl))phenoxy)hexan-1-ol (2.000 g, 0.007 mol) was dissolved in 2-butanone (MEK, 15 mL), after which 2-isocyanatoethyl acrylate (1.976 g, 0.014 mol) was added to the solution. After mixing for 20 min at ambient temperature, dibutyltin dilaurate (DBTDL, 0.019 g) was added, and the mixture was heated for reaction (40 °C, 6 h). The reaction proceeded under nitrogen purging conditions. The product was precipitated using n-hexane, and the desired product, namely azo acrylate (2-((((6-(4-(phenyldiazenyl)phenoxy)hexyl)oxy) carbonyl)amino)ethyl acrylate), was obtained by vacuum drying.

In the final step, an azobenzene-based acrylic polymer was synthesized by the polymerization of butyl acrylate and azo acrylate. Before polymerization, the butyl acrylate inhibitor was removed using neutral aluminum oxide (Sigma-Aldrich). Butyl acrylate (1.5 g, 0.012 mol), azo acrylate (0.572 g, 1.3 mmol), and ethyl acetate (EAc, 5 mL) were mixed for 1 min at 70 °C. The solution was purged with nitrogen gas for 20 min at 25 °C, after which 2,2'-azobisisobutyronitrile (AIBN, 0.01 g) was added. The polymerization proceeded at 70 °C for 90 min. After polymerization, tetrahydrofuran (5 mL) was added to prevent azobenzeneinduced gelation. The unreacted acrylic monomer was washed three times with methanol. The final product was obtained by drying the washed solution in film form at 70 °C. The chemical structures of the synthesized compounds were verified by <sup>1</sup>H NMR (Fig. S2a).

# 2.2.2. Synthesis of azobenzene compounds

Azobenzene compounds without urethane bonds (Azo-C10) were prepared using the following reaction (Fig. S1b). First, 4-phenylazophenol (1.982 g, 0.010 mol), potassium carbonate (1.382 g, 0.010 mol), and DMF (9 mL) were mixed. Subsequently, potassium iodide (4.2 mg, 0.025 mmol) and 1-chlorodecane (0.015 mol) were added to the solution, and the reaction proceeded at 110 °C for more than 24 h. After the reaction, the product was precipitated using cold water and refined by recrystallization in n-hexane. The desired product was obtained via filtration and vacuum drying. The synthesis procedure for Azo-C14 was similar to that described above. However, 1-chlorotetradecane was used instead of 1-chlorodecane. In addition, Azo-C14 was recrystallized in acetone instead of n-hexane.

The procedure for the preparation of azobenzene compounds containing urethane bonds (Azo-U12) is shown in Fig. S1c. First, 6-(4-(phenyldiazenyl)phenoxy)hexan-1-ol was dissolved in MEK (15 mL) at ambient temperature. Subsequently, hexyl isocyanate (1.272 g, 0.010 mol) was added, and the solution was purged with nitrogen gas for 20 min. Next, the reaction was started by adding DBTDL (0.019 g) and heating (60 °C, 6 h). The product was precipitated using cold n-hexane, and the final product (6-(4-(phenyldiazenyl)phenoxy) hexylcarbamate) was obtained by vacuum drying. The chemical structures of the synthesized compounds were verified by  ${}^{1}$ H NMR (Figs. S2b and S2c).

#### 2.2.3. Preparation of switchable adhesives

The switchable adhesive was prepared as a film using the following steps: First, the azobenzene-based acrylic polymer (0.1 g) was dissolved in tetrahydrofuran (1 mL). The azobenzene compounds, namely Azo-C10, Azo-C14, and Azo-U12, were mixed with the azobenzene-based acrylic polymer solution. The content of azobenzene compounds was fixed as 12 mol%. The resulting switchable adhesive comprised 80.7 mol%, 7.3 mol%, and 12 mol% of butyl acrylate, azo acrylate, and azobenzene compound. Next, the mixture was coated on a polyethylene terephthalate (corona-treated surface, 50  $\mu$ m thick) film using a 120  $\mu$ m thick applicator. The coated film was dried at 100 °C for 20 min; the final thickness of the switchable adhesive was 6–7  $\mu$ m. The initial state of the switchable adhesives was deactivated simultaneously by transforming all azobenzene moieties through irradiation with visible light (50 W white LED lamp, 30 s), followed by UV light (365 nm LED lamp, 125 mW/cm<sup>2</sup>, 30 s).

# 2.3. Characterization

# 2.3.1. Adhesion test

The switchable adhesive was dried on a release film and transferred to a glass substrate. Subsequently, a steel probe was made to approach the adhesive at a fixed speed (0.2 mm/s) and press the adhesive film (1 N for 1 s). Subsequently, the force generated by the probe was detached at a constant speed of 10 mm/s, and the results were recorded. The probe tack refers to the maximum force required to detach the steel probe from the adhesive film.

# 2.3.2. UV-pulsed laser system

A diode-pumped solid-state laser (DX-355-15, Photonics Industries) was employed for the UV-pulsed laser system (Fig. S3). The wavelength, pulse width, and repetition rate were 355 nm, 19 ns, and 90 kHz, respectively.

# 3. Results and discussion

# 3.1. Design strategy

Our previous study showed that azobenzene composites consisted of an azobenzene-based polymer, and the compound exhibited a remarkable adhesion-switching behavior (Fig. 2a) [27]. The adhesion switching was achieved by photoisomerizing azobenzene-based polymers and azobenzene compounds, and their photoisomerization behaviors were already characterized in previous research [27,28]. The switching behavior depends on the side chain length of the azobenzene compound, which can be attributed to variations in both the crystallinity and free volume. Specifically, previous results indicated that a minimum side chain length is necessary to enable effective adhesion switching behavior, whereas an excessively long side chain can result in a slow response to UV and reduced adhesive force under activated conditions [28]. In other words, adhesion activation and deactivation behaviors were previously adjusted by the side chain length of the azobenzene compound. However, in this study, we designed a novel azobenzene compound consisting of functional linkages, a urethane bond, rather than conventional C-C linkages. We expected that azobenzene compounds containing urethane bonds would be the best candidates for satisfying the requirements above. Incorporating urethane bonds was expected to enhance the photoisomerization rate of the azobenzene moieties by increasing the free volume and improving the adhesive force via hydrogen bonding with the adherend.

Laser irradiation at high power induces surface deformation in the switchable adhesive; a straightforward approach to mitigating this effect



**Fig. 2.** (a) Composition of an azobenzene-based switchable adhesive (Figs. S1 and S2). (b) Testing procedure for the adhesive force of switchable adhesives. Adhesion switching testing with (c) UV (activation of adhesion, 365 nm, 5 s) and (d) visible light exposure (deactivation of adhesion, 50 W white LED lamp, 30 s). The energy density ( $J/cm^2$ ) was calculated as the product of the UV intensity ( $W/cm^2$ ) and irradiation time (5 s). The content of the azobenzene compounds (Azo-C10, Azo-C14, and Azo-U12) was fixed as 12 mol%. SONGOSRB® 1000 was used as a UV absorber, and its content was fixed at 30 mol%.

involves reducing the laser power. However, such a power reduction inevitably results in a diminished adhesion switching rate. To address this problem, a promising solution involves the precise modulation of laser absorption on a switchable adhesive surface with additives, such as UV absorbers. Furthermore, given that heat can mitigate surface deformation [34], it is reasonable to anticipate a similar effect of heat generated by the UV absorber in suppressing such deformations. There are several types of UV absorbers, including benzotriazole, triazine, benzophenone, formamidine, oxanilide, and cyanoacrylate [37]. In this study, 2-(2-hydroxy-5-methylphenyl)benzotriazole (SONGSORB®1000, Fig. 2a) was used because of its high absorption at 355 nm (Fig. S4).

#### 3.2. Adhesion switching via a UV LED lamp

Prior to examining the laser-induced adhesion switching, the switching characteristics were evaluated using a UV LED lamp, and the adhesive force was evaluated using a probe tack test, as shown in Fig. 2b. First, a switchable adhesive film was transferred to a glass substrate and exposed to UV (365 nm, 5 s) or visible light (50 W white LED lamp, 30 s). Then, a steel probe was made to approach the switchable adhesive at a speed of 0.2 mm/s and pressed under a constant force (1 N) for 1 s. The probe tack was determined as the maximum force exerted during the detachment of the steel probe at a constant speed of 10 mm/s.

The augmentation of the UV intensity led to an increase in the

adhesion force of the switchable adhesives, indicating the activation (or switch-on) of adhesion (Fig. 2c). The switching behavior was significantly influenced by additives, particularly azobenzene compounds and UV absorbers. As previously reported by our group [28], the activation of adhesion was observed at lower energy densities through a reduction in the side chain length of the azobenzene compound. This reduction in length led to a decrease in crystallinity and an increase in the free volume (Fig. S5), promoting photoisomerization [38]. However, the shortened side chains resulted in a discernibly slower deactivation rate (Azo-C10 in Fig. 2d), which significantly affected the processing rate of the mini/micro-LED transfer. These results demonstrate that modifying the side-chain length of an azobenzene compound alone cannot simultaneously achieve rapid activation and deactivation.

To address this issue, we used a urethane-modified azobenzene compound (Azo-U12). Fig. 2c and d show that Azo-U12 exhibited a rapid activation comparable to Azo-C10 but with a significantly faster deactivation rate. These findings can be explained by two mechanisms. First, the urethane bond in the azobenzene compound reduced its crystallinity (Fig. S5), facilitating the photoisomerization of the azobenzene moiety. Second, incorporating Azo-U12 into the switchable adhesives resulted in liquid crystalline behavior (Fig. S5), which is essential for excellent switching on/off behavior at room temperature [6,31]. Furthermore, as hypothesized, the adhesive incorporating Azo-U12 exhibited a significantly greater adhesion force than that of Azo-C14, which was attributed

to intramolecular forces induced by urethane, such as hydrogen bonding.

We also examined the impact of the UV absorber on the adhesionswitching behavior. The activation rate of adhesion was unexpectedly enhanced upon the incorporation of a UV absorber (Fig. 2c). The observed reduction in the melting enthalpy suggests that the presence of the UV absorber may have disrupted crystal formation (Fig. S6).

#### 3.3. Adhesion switching via a UV-pulsed laser

Next, we utilized a UV-pulsed laser to achieve prompt and precise activation of switchable adhesives. Activated adhesion strength should be characterized under the same irradiation time to compare the switching behavior between conventional UV and laser. However, in the case of a UV laser, its beam size (40–100  $\mu$ m) was too small that it was required to overlap the laser beam to activate a sufficiently large area for adhesion assessment in a single exposure (Fig. 3a). Although this overlap made it difficult to quantitatively compare the speed of adhesion activation between conventional UV and laser, it enabled the evaluation of adhesion assessment to optimize the condition of laser exposure. The beam size was determined by the defocusing length, and the pitch was fixed as the beam size, whereas the overlap rate was obtained through computation using Equation (1).

Overlap rate = 
$$\frac{\text{Repetition rate } (H_z) \times \text{Beam size } (\mu \text{m}) \times 10^3}{\text{Scan speed } (\text{mm/s})},$$
 (1)

To determine the pulse energy density of a UV-pulsed laser, we need to consider its power and factors such as the repetition rate and beam size. The energy density can be calculated by multiplying the pulse energy density by the overlap rate according to Equation (2).

$$Energy density (J/cm2)$$
= Pulse energy density (J/cm<sup>2</sup>) × Overlap rate
Power (W)
Repetition rate (kHz) × Beam area (mm<sup>2</sup>) × Overlap rate,
(2)

Multiple exposure conditions were devised to optimize the laserinduced activation of switchable adhesives, wherein the power of the UV pulse laser was varied between 10, 20, and 25 mW, and the energy density was systematically adjusted across the range  $0.01-7.96 \text{ J/m}^2$ (Table 1).

After establishing the UV-pulsed laser exposure conditions, we investigated the activation behavior of the two switchable adhesives, Azo-C14, and Azo-U12 with a UV absorber, as illustrated in Fig. 3b. Notably, the adhesive strength of the switchable adhesive containing Azo-U12 and the UV absorber significantly increased at a scan speed of 0.036 m/s, whereas the adhesive strength of the Azo-C14-based switchable adhesive remained unchanged. We attributed this outcome



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Fig. 3. a) Schematic illustration of a UV-pulsed laser. b) Adhesive strength according to the scan speed. The power and pulse energy density were fixed at 20 mW and 7.86 mJ/cm<sup>2</sup>, respectively. The additive content was fixed at 12 mol% for both Azo-C14 and Azo-U12. The UV absorber (SONGSORB® 1000) content was set as 30 mol%. c) Surface images after UV-pulsed laser exposure (ECLIPSE LV100ND, Nikon). d) Adhesive strength as a function of the energy density. The power of the laser was set to 10, 20, and 25 mW. Azo-U12 (12 mol%) and a UV absorber (30 mol%, SONGSORB® 1000) were used as additives.

Table 1Exposure conditions of the UV-pulsed laser.

No.	Repetition rate (kHz)	Power (mW)	Beam size (µm)	Scan speed (m/s)	Overlap rate	Pulse energy density (mJ/m <sup>2</sup> )	Energy density (J/m <sup>2</sup> )
1	90	10	100	1	9	1.42	0.01
2				0.1	90		0.13
3				0.01	900		1.27
4			80	0.8	9	2.21	0.02
5				0.08	90		0.20
6				0.008	900		1.99
7			60	0.6	9	3.93	0.04
8				0.06	90		0.35
9				0.006	900		3.54
10			40	0.4	9	8.85	0.08
11				0.04	90		0.80
12				0.004	900		7.96
13	90	20	60	0.012	450	7.86	3.54
14				0.024	225		1.77
15				0.032	169		1.33
16				0.034	159		1.25
17				0.036	150		1.18
18				0.038	142		1.12
19				0.040	135		1.06
20				0.048	112		0.88
21	90	25	60	0.012	450	9.83	4.42
22				0.024	225		2.21
23				0.036	150		1.47
24				0.048	112		1.10
25				0.060	90		0.88
26				0.072	75		0.74
27				0.084	64		0.63

to the optomechanical stress-induced surface deformation, which was more pronounced in the case of the Azo-C14-based switchable adhesive, as depicted in Fig. 3c. However, such surface deformation was hardly observed when Azo-U12 and a UV absorber were used. We hypothesized that the heat generated by light absorption by the UV absorber could relieve the optomechanical stress and reduce surface deformation. However, we observed minimal thermal effects because the addition of 30 mol% of UV absorber did not significantly alter the temperature (Fig. S6). Conversely, we speculated that the precise modulation of light absorption by the UV absorber played a crucial role in mitigating optomechanical stress-induced surface deformation. Nevertheless, the adhesive strength decreased under low-scan-speed conditions despite applying the UV absorber (Fig. 3b). This decline was speculated to result from surface damage caused by excessive light irradiation. However, no explicit confirmation of such damage was obtained by microscopic imaging (Fig. 3c and S8).

The strength of the activated switchable adhesive was assessed by varying the power and energy densities of the UV-pulsed laser (Fig. 3d). Our results revealed that an increased energy density improved the adhesive strength at a laser power of 10 mW. A similar trend was observed for the UV LED lamps. However, the activation required a considerably higher energy density with laser-induced activation. Moreover, the adhesive strength of the activated adhesive was inferior to that of the UV LED lamps, which could be attributed to the inadequate photoisomerization of the azobenzene moiety owing to the short exposure time. When the laser power was increased to 20 mW, the adhesive strength increased sharply as a function of the energy density. However, a rapid decrease was observed at higher energy densities. A high energy density can cause problems such as laser ablation or optomechanical stress-induced deformation. Similarly, an initial increase, followed by a decrease in the adhesive strength, was observed in the energy density at a laser power of 25 mW. Furthermore, with an increase in laser power, particularly at 25 mW, a poor adhesive strength lower than 0.5 N was observed, indicating insufficient activation of the switchable adhesive. Consequently, the optimal power and energy density conditions for exposure with a UV-pulsed laser were determined to be 20 mW and 1.18 J/cm<sup>2</sup>, respectively.

3.4. Selective transfer of a mini-LED via UV-pulsed laser-induced switching

After optimizing the switchable adhesive composition (12 mol% of Azo-U12 and 30 mol% of the UV absorber) and laser exposure conditions (power: 20 mW, energy density: 1.18 J/cm<sup>2</sup>), a four-step process was implemented to achieve selective transfer of the mini-LED (Fig. 4). Initially, the switchable adhesive was selectively activated by exposure to a UV-pulsed laser, with an activated area of 300  $\mu m \times 300 \ \mu m$  and a distance of 4 mm between activated regions. The laser was scanned at a high speed (1-2 m/s), facilitating rapid adhesion activation with excellent selectivity in a second. Subsequently, the selectively activated switchable adhesive was positioned on a moving plate and brought into contact with the glass that contained the mini-LED (size: 100  $\mu m \times 200$ µm, distance between mini-LEDs: 2 mm). The contact between the adhesive and mini-LED was observed under a microscope. The next step involved confirming that the mini-LED was successfully transferred onto the switchable adhesive. The distance between the transferred mini-LED was confirmed to be 4 mm, indicating a successful selective transfer. This result indicated that the prepared switchable adhesive exhibited sufficient adhesive strength to transfer the mini-LED under the optimized exposure conditions of the UV-pulsed laser. Finally, the mini-LED was successfully transferred to PDMS by exposure to visible light. These results clearly demonstrate that the mini-LED was selectively transferred using an azobenzene-based switchable adhesive prepared by UV-pulsed laser exposure.

We firmly believe that this study holds promise in expanding the applicability of laser-induced selective transfer for mini-LEDs. However, three crucial aspects warrant future attention. Firstly, the transfer rate and spacing between LED chips must be analyzed. While our work demonstrated successful laser-induced switching using azobenzene-based switchable adhesive, achieving a faster transfer rate and reducing LED intervals is imperative for ensuring commercial viability. The UV-pulsed laser with nanoseconds we used in this paper is expected to facilitate the fast and accurate transfer with micrometer level intervals thanks to its small beam size (40–100  $\mu$ m), high resolution (<1  $\mu$ m) and prevention of thermal issues. Secondly, efforts should be directed towards broadening the range of substrates that accept LED



Fig. 4. Schematic illustration of the selective transfer procedure of mini-LEDs using the prepared switchable adhesive. The adhesive contained 12 mol% of Azo-U12 and 30 mol% of a UV absorber (SONGSORB® 1000). The power and energy density of the UV-pulsed laser were set as 20 mW and 1.18 J/cm<sup>2</sup>, respectively.

chips. Our findings indicated that mini LED transfer was only successful on PDMS substrates due to their adhesive properties, whereas Si wafers and glass proved less receptive. Generally, the surface of panels or Si wafers has been usually modified by flux to be tacky for readily accepting the micro-LED chips. It is necessary to optimize the tackiness of substrates accepting LED chips in the future. Thirdly, the durability of the azobenzene composites-based switchable adhesive requires enhancement. While our prior work showcased the excellent durability of the adhesive under 30 cycles of UV and visible light exposure [27,28], laser-induced switching could only last 5 cycles (Fig. S9). Further investigation is crucial to ensuring the reusability of the switchable adhesive.

# 4. Conclusion

This study developed a switchable adhesive based on azobenzene composites for the selective transfer of mini-LEDs using laser-induced techniques. The newly designed urethane-functionalized azobenzene compound exhibited excellent adhesion activation under UV light and rapid deactivation under visible light. It was established that the addition of a UV absorber mitigated the laser-induced surface deformation of azobenzene-based composites, leading to a higher adhesive strength than that of composites without a UV absorber. Furthermore, the relationship between the laser power and adhesion activation behavior was determined, and the optimal conditions were identified (power: 20 mW, energy density: 1.18 J/cm<sup>2</sup>). Finally, the azobenzene composite-based switchable adhesive enabled the laser-induced selective transfer of mini-LEDs. This finding broadens the scope of laser-induced adhesion switching and lays the foundation for extending the range of applications of azobenzene-based switchable adhesives.

#### CRediT authorship contribution statement

Tae-Hyung Lee: Conceptualization, Investigation, Methodology, Writing – original draft. Jong-Ho Back: Funding acquisition, Methodology, Writing – original draft. Jae-Seung Lim: Investigation, Methodology. Gi-Yeon Han: Conceptualization. Mo-Beom Yi: Investigation. Youngdo Kim: Methodology. Jae-Hak Lee: Methodology. Seungman Kim: Supervision, Writing – review & editing. Hyun-Joong Kim: Supervision, Writing – review & editing.

# Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesb.2023.111175.

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