

Effect of UV-LED Illuminant on the Curation of Photolent-amidine Mixed with Bisphenol A Epoxy Acrylate under Printing Conditions

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Abstract. In order to make photocuring ink or coating cured by UV-LED illuminant, we synthesized (4-((hexahydropyrrolo[1,2-a]pyrimidin-1(2H)-yl)methyl)phenyl)(phenyl)methanone(PL -DBN) and (4-((octahydropyrimido[1,2-a]azepin-1(2H)-yl)methyl)phenyl)(phenyl)methanone(PL -DBU) as photoinitiators. Different mass fraction of the photoinitiators was mixed with bisphenol A epoxy acrylate, cured by different wavelengths and power of UV-LED illuminant, and investigated the curing effects of photoinitiators on bisphenol A epoxy acrylate. The results show that the conversion of C=C double bonds of bisphenol A epoxy acrylate will increase as the mass fraction of the photoinitiators or the power of UV-LED illuminant increase. In the same conditions, the curing effect of using 365nm UV-LED illuminant on bisphenol A epoxy acrylate is better than using 395nm UV-LED illuminant. PL-DBU has a better curing effect on the bisphenol A epoxy acrylate rather than PL-DBN. When using the 8W/cm² of 365nm UV-LED illuminant to cure a mixture of 3% PL-DBU and 97% bisphenol A epoxy acrylate, it will be dry completely in 2 seconds, moreover, the conversion reach 79%.

Keywords: (4-((hexahydropyrrolo[1,2-a]pyrimidin-1(2H)-yl)methyl)phenyl)(phenyl)methanone; UV-LED illuminants; (4-((octahydropyrimido[1,2-a]azepin-1(2H)-yl)methyl)phenyl)(phenyl)methanone; photolent-amidine; photoinitiators

1 Introduction

Photolent bases are the new photoinitiators that can generate nitrogenous bases active substance after ultraviolet(UV) irradiation. Photolent bases are not affected by oxygen inhibition and moisture, and widely used for UV curing. It has a very broad application prospects and become a hot research photoinitiator^[1-3]. Photolent bases consist of chromophores and tertiary amine precursors. Chromophores are part of the photolent bases, which absorb photon energy from UV rays. Tertiary amine precursors are nitrogenous bases active substance that play a part in catalytic polymerization of unsaturated resins. Kutal synthesized in the history of the first photolent bases, which is the cobalt ammonia complex, which can generate nitrogenous bases active substance that was used as a

crosslinking agent in the curing of epoxy resin^[4,5]. Liu introduced four kinds of chromophores on secondary nitrogen atom of octahydropyrrolo[1,2-a]pyrimidine and decahydropyrimido[1,2-a]azepine, synthesized eight photolabile-amidine with photochemical activity, and research the properties of free-radical photopolymerizations and base catalysis of them^[6]. UV-LED illuminants have excellent environmental protection and energy saving property, gradually replace the traditional high pressure UV mercury lamp. UV-LED illuminants have a single radiative peak normally, and the irradiation intensity of UV-LED illuminants is weak^[7]. Therefore, the curing speed of the normal UV photocurable coating and UV curable inks is slow, and the curable thickness of them is small. As a result, the normal photoinitiators can't meet the industrial production requirements.

According to reducing dicyclic amidine, and then two photolabile-amidine photoinitiators were obtained by nucleophilic substitution reaction, which are (4-((hexahydropyrrolo[1,2-a]pyrimidin-1(2H)-yl)methyl)phenyl)(phenyl)methanone(PL-D BN) and (4-((octahydropyrimido[1,2-a]azepin-1(2H)-yl)methyl)phenyl)(phenyl)methanone(PL-DBU). In order to investigate the curing effect of the photoinitiators on bisphenol A epoxy acrylate resin in UV-LED illuminant, we selected different mass fraction of the photoinitiators to mix with bis-phenol A epoxy acrylate resin. The mixture was cured by different wavelengths and power of UV-LED lamps.

2 Experimental Section

2.1 Experimental Materials and Instruments.

The main experimental materials listed in table1, and the main experimental instruments listed in Tab2.

TABLE1. INFORMATION OF EXPERIMENTAL MATERIALS

Raw Materials	Mark	Purity	Provider
1,5-diazabicyclo[4.3.0]non-5-ene	-	AR	Shandong Wanbo Chemical Reagent Co,Ltd
1,8-diazabicyclo[5.4.0]undec-7-ene	-	AR	Shandong Wanbo Chemical Reagent Co,Ltd
4-methylbenzophenone	-	AR	Xiya Reagent
benzoyl peroxide	-	AR	Xiya Reagent
N-bromobutanamide	-	AR	Xiya Reagent
lithium aluminum hydride	-	AR	Xiya Reagent
tetrahydrofuran	-	AR	Tianjin Kemiou Chemical Reagent Co,Ltd
bisphenol A epoxy acrylate	9105B-80	20%TPG DA	Jiangmen Hengguang New materials Co,Ltd

TABLE2. INFORMATION OF EXPERIMENTAL INSTRUMENTS

Instruments	Model	Provider
FTIR Sepctrometer	FTIR-8400	Shimadzu
UV-LED illuminants	365nm/395nm	Shenzhen Weihailixin Technology development co.,LTD
Printability tester	C1	IGT Testing Systems

2.2 Organic Synthesis.

0.1mol 1,5-diazabicyclo[4.3.0]non-5-ene and 150mL tetrahydrofuran were added to a 500ml 3-neck round bottom flask, and then the mixture was heated under reflux for 2h in the temperature range 90°C to 100°C. 0.1mol Lithium aluminum hydride was added to the flask step by step during the heating period. Whereafter, the mixture was stirred for 24h at room temperature. Then the mixture was cooled to 8°C in an ice bath. We added 10ml saturated solution of ammonia chloride to the mixture, filtered out the sediment, removed the moisture by using sodium sulfate, at last, evaporated the organic solvent. As a result, octahydropyrrolo[1,2-a]pyrimidine(RDBN) was obtained.

0.1mol 1,8-diazabicyclo[5.4.0]undec-7-ene and 150mL tetrahydrofuran were added to a 500ml 3-neck round bottom flask, and then the mixture was heated under reflux for 2h in the temperature range 100°C to 110°C. 0.1mol Lithium aluminum hydride was added to the flask step by step during the heating period. Whereafter, the mixture was stirred for 24h at room temperature. Then the mixture was cooled to 8°C in an ice bath. We added 10ml saturated solution of ammonia chloride to the mixture, filtered out the sediment, removed the moisture by using sodium sulfate, at last, evaporated the organic solvent. As a result, decahydropyrimido[1,2-a]azepine(RDBU) was obtained.

0.12mol 4-methylbenzophenone(MBP)、200ml carbon tetrachloride、0.1mol N-bromobutanamide(NBS) and 0.1mol benzoyl peroxide(BPO) were added to a 500ml 3-neck round bottom flask, and then the mixture was heated under reflux for 1h in the temperature range 90°C to 95°C. Then we filtered the mixture after it was cooled to room temperature. Subsequently, removed carbon tetrachloride from the mixture, and added 100mL alcohol to the mixture. Thereout, 4-(bromomethyl)benzophenone(Br-MBP) was obtained by recrystallization.

150ml methylbenzene、0.3mol RDBN and 0.3mol Br-MBP were added to a 500ml 3-neck round bottom flask, and then the mixture was heated under reflux for 24h in the temperature range 80°C to 90°C. After separation and purification, we finally got 4-((hexahydropyrrolo[1,2-a]pyrimidin-1(2H)-yl)methyl)phenyl)(phenyl)methanone(PL-DBN). In a same way, we got 4-((octahydropyrimido[1,2-a]azepin-1(2H)-yl)methyl)phenyl)(phenyl)methanone(PL-DBU).

2.3 Samples and Their Text.

The mass fraction of 1%,2%,3%,4% of photolatent-amidine photoinitiators were mixed with bisphenol A epoxy acrylate respectively. Stirred the mixture to make it uniform. Then

sampled the 0.1cc mixture, and smeared it on the binary roller of printability tester. Opened the printability tester and printed on the copper printing paper. As a result, a series of 30*30mm printed samples were obtained.

The samples were exposed to the dominant wavelength of 365nm and 395nm UV-LED illuminants. Intermittent infrared spectroscopy was adopted to evaluate the curing rate of the conversion of C=C double bonds^[8,9]. The C-H bonds faces to the peak of bending vibration on the 810cm⁻¹ of C=C double bonds in the spectrum, and its absorption intensity decreases as UV irradiation time increases. The conversion of C=C double bonds was calculated according to the following equation where A₀ is the absorption intensity on the 810cm⁻¹ of C=C double bonds without UV irradiation, A_t is the absorption intensity on the 810cm⁻¹ of C=C double bonds after UV irradiation, C_t is the conversion of C=C double bonds, respectively.

$$C_t = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

3 Results and Discussion

3.1 Organic Synthesis.

Figure1 shows the synthetic routes of the photolatent-amidine. According to reducing dicyclic amidines, we got alkalinescent RDBN and RDBU. Then chromophore was introduced at secondary nitrogen atoms of RDBN and RDBU by nucleophilic substitution reaction. As a result, the photolatent-amidine were obtained. The product yields and purity of all the products show Tab3.

TAB3. THE PRODUCT YIELDS AND PURITY OF ALL THE PRODUCTS

Products	Br-MBP	RDBN	RDBU	PL-DBN	PL-DBU
Products Yields (%)	64	58	55	42	39
Purity (%)	99.1	98.3	97.8	95.2	93.3

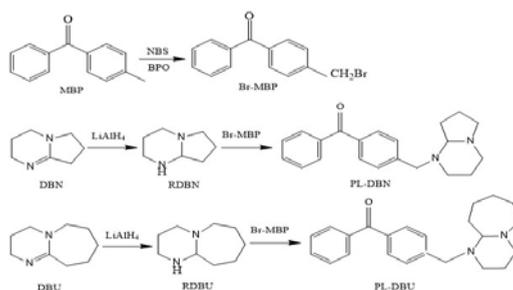


Figure1. The synthesis routes of photolatent-amidine

As shown in Figure2, photon energy excites the photolatent-amidine molecules into another excited state, the C-N bond that chromophore connect with amidine will break and generate free radicals^[10-12]. The hydrogen atom on the tertiary carbon of the amidine is

activated by the two ortho nitrogen atoms, and then the hydrogen atom will be picked up by the chromophore free radical. Consequently, the tertiary carbon and secondary nitrogen on the amidine will combine into C=N double bond, in other words, generate DBN at last. In the same principles, PL-DBU can release DBU by absorbing photon energy. Because the conjugated degree of 4-methylbenzophenone is high, correspondingly, its derivatives will lead to red shift.

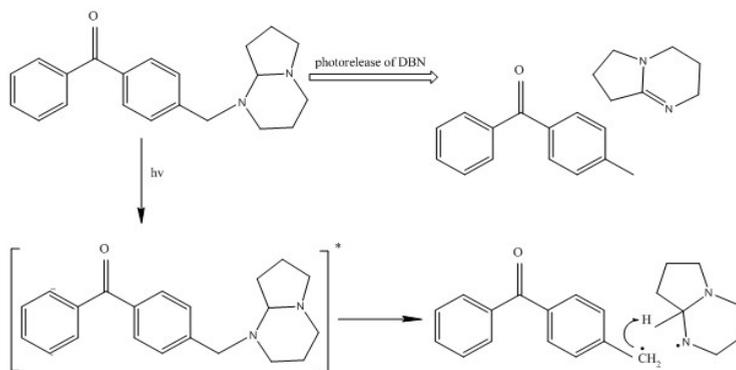


Figure2. Photochemical reaction of PL-DBN

3.2 Mass Fraction of Photoinitiators.

Different mass fraction of photoinitiators was added into a certain amount of bisphenol A epoxy acrylate and made into samples. The samples were exposed to $6\text{W}/\text{cm}^2$ of the dominant wavelength of 365nm and 395nm UV-LED illuminant for 3 seconds. Intermittent infrared spectroscopy was adopted to test the conversion of C=C double bonds of the resin. The results show Figure3.

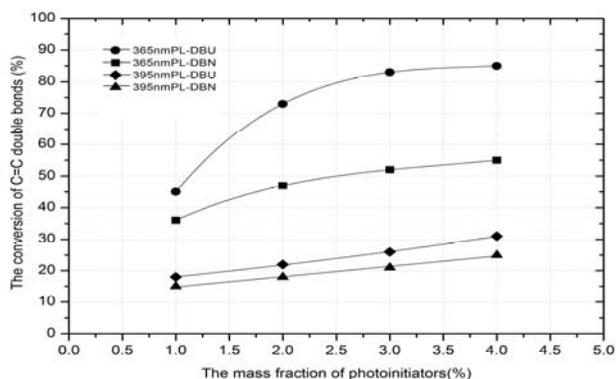


Figure3. The conversion of C=C double bonds with different mass fraction of photoinitiators

As shown in figure3, the conversion of C=C double bonds of bisphenol A epoxy acrylate increases as the mass fraction of photoinitiators increases in the same UV-LED illuminant. The light absorbency A is calculated according to the following equation

$$A = \log(I_0 / I) = \kappa lc \quad (2)$$

where I_0 is the intensity of the incident radiation, I is the intensity of transmitted radiation, κ is the molar absorption coefficient, l is the thickness of the sample, c is the mole concentration of the sample. κ is a certain constant, and l is also a certain constant when the experiment conditions is same. When the mass fraction of photoinitiator increases, the mole concentration gradually become larger. It also means that the light absorbency is directly proportion to the mass fraction of photoinitiators^[13-15]. Under the certain UV-LED irradiation, photoinitiators absorb less the energy of ultraviolet ray and generate less tertiary amine precursors at a lower mass fraction, as a result, the curing effect is unsatisfactory. It will be conducive to absorb the energy of ultraviolet ray and generate more tertiary amine precursors when the mass fraction of photoinitiators is increasing from 1% to 3%. The surface of the resin absorb almost ultraviolet ray so that the radiant flux inside ink is few. Generating the amount of nitrogenous bases inside is directly proportion to the mass fraction of photoinitiators and the light flux. Therefore, the conversion of C=C double bonds will flatten out after the UV-LED illuminant irradiated the samples for a period of time.

In the same conditions, the conversion of C=C double bonds of PL-DBU/bisphenol A epoxy acrylate is larger than PL-DBU/bisphenol A epoxy acrylate. When the resin solidifies slowly, the ability of anti-oxygen inhibition become the main factors influencing the curing effects of the resin^[16,17]. From the point of view of molecular astructure, the steric hindrance of PL-DBU is smaller than PL-DBN. It is to say that PL-DBU has the better ability of anti-oxygen inhibition, in favor of radical termination reaction^[18,19]. As a conclusion, PL-DBU is more suitable for curing bisphenol A epoxy acrylate.

3.3 Wavelength of UV-LED Illuminant.

As shown in Figure3, in the same conditions, 365nm UV-LED illuminant is more suitable for curing PL-DBU/bisphenol A e epoxy acrylate than 395nm UV-LED illuminant. The photon energy is determined as

$$E = \frac{hc}{\lambda} \quad (3)$$

where h is Planck constant, c is the velocity of light, λ is the wavelength of light. Because h and c are certain constants, the shorter the wavelength, the higher the energy. Breaking the C-N bond that chromophore connect with amidine need to absorb the energy of ultraviolet ray. Therefore, the shorter the wavelength, the more beneficial to break the C-N bond and generate more active bases to improve curing speed and effect.

We found that the surface of the mixture could be dry completely when the conversion of C=C double bonds of bisphenol A epoxy acrylate reached 78% in the experiment. In other words, if the conversion is above 78%, it can realize dry completely. When the samples were exposed to 365 nm UV-LED illuminant for 3 seconds, the conversion of C=C double bonds increase rapidly as the mass fraction of PL-DBU increases from 1% to 3% and increase slowly as the mass fraction of PL-DBU is above 3%. When the sample that the mass fraction of PL-DBU is 3%, exposed to the 6W/cm² of 365nm UV-LED illuminant for 3 seconds, it will realize completely dry and the conversion reach 82%.

3.4 Irradiation Intensity of UV-LED Illuminant.

In order to investigate the influence of irradiation intensity of UV-LED illuminants on the curing effect of PL-DBU/bisphenol A epoxy acrylate, a mixture of 3% PL-DBU and

97% bisphenol A epoxy acrylate is exposed to $4\text{W}/\text{cm}^2$, $6\text{W}/\text{cm}^2$, $8\text{W}/\text{cm}^2$ and $10\text{W}/\text{cm}^2$ of 365 nm UV-LED illuminants for different time, respectively. Test results were shown in Figure4.

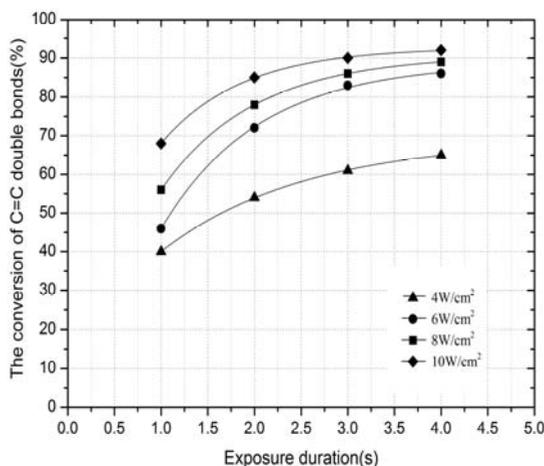


Figure4. The conversion of C=C double bonds with different exposure duration

While the irradiation intensity of UV-LED illuminants is increasing, the conversion of C=C double bonds of bisphenol A epoxy acrylate is increasing, and the curing speed is improving. Because more ultraviolet rays reach ink film inside, it can effectively improve the curing speed and effect. When the sample contains 3% PL-DBU, exposed to the $8\text{W}/\text{cm}^2$ of 365nm UV-LED illuminant for 2 seconds, it will realize completely dry and the conversion reach 79%.

4 Summary

In the same UV-LED illuminant, the conversion of C=C double bonds of bisphenol A epoxy resin acrylate increases with the mass fraction of photoinitiators. In the same conditions, the curing effect of PL-DBU on bisphenol A epoxy acrylate is better than PL-DBN, using 365nm UV-LED illuminant is more suitable for curing a mixture of PL-DBU and bisphenol A epoxy acrylate than 395nm UV-LED illuminants. Improving the irradiation intensity of UV-LED illuminants is beneficial for improving the curing speed and effect. When using the $8\text{W}/\text{cm}^2$ of 365nm UV-LED illuminant to cure a mixture of 3% PL-DBU and 97% bisphenol A epoxy acrylate, it will be dry completely in 2 seconds, moreover, the conversion reach 79%.

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