Study on Curing Speed of UV-LED Inkjet Ink

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Abstract

In order to improve the curing speed of UV-LED inkjet ink, different types of prepolymers, monomers, photoinitiators were used to prepare ink, then the inks were cured under 365nm UV-LED illuminant to investigate their impact on curing speed. Co-photoinitiators were designed by formulation experiment and the content of photoinitiator was changed to make ink samples, after curing speed being tested, the photoinitiator and its content were determined which can obtain higher curing rate. In addition, the single-core, dual-core and quad-core UV-LED illuminant were used to cure the same ink and test their curing speed. The results show that the prepolymer, the structure of monomer, the content of photoinitiator and its light absorption, the parameters of illuminant all have a significant impact on UV-LED inkjet ink, the prepared inks match the illuminant can have higher curing speed.

Introduction

UV curing refers to the curing materials absorb a certain band of ultraviolet and then occur cross-linking polymerization reaction after UV irradiation, which is the process from the liquid into the solid state [1]. Conventional UV light source is high-pressure mercury lamp, and it has the defects such as short life, high power consumption, deformation of printing materials and heavy metal pollution [2]. However, UV-LED utilized the photoelectric conversion principle to apply voltage at the polarity direction of the chip, to make the electron and the positive charge have collisions and combinations in the chip in the process of moving which can transform the energy into light [3]. Compared with traditional UV source, UV-LED has the advantages such as longer life, smaller thermal deformation of the substrate, higher efficiency and energy saving, faster reaction speed and so on [4].

Curing velocity is one of important properties of UV-LED ink-jet ink, which decides the printing speed. As UV-LED light has single radiation peak, and the energy gathers in a narrow spectral band of ultraviolet light, while the spectral power density is high in the band area. The power of UV-LED light in market is low, so, improve curing velocity is the most urgent problems to be resolved of UV-LED ink-jet ink, which can provide effective help for development of the ink

Experiment

Experimental Materials

Prepolymer: CN2302, CN2303, 6361-100; Monomer: EOEOEA, HDDA, NPGDA, TPGDA, DPGDA, EO3-TMPTA, TMPTA; Photoinitiator: ITX, 369, TPO, 907, 819; Pigment: Phthalocyanine blue; Addictives: EHA, 9077.

Experimental Equipments

High speed grinder (GJ-2S, China); Mechanical stirrer (JJ-I, China); Temperature magnetic stirrer (Jiangsu Ronghua Machines Co., Ltd); UV-Vis spectrophotometer (UV-2501PC, Japan); Fourier transform infrared spectrometer (FTIR-8400, Japan); UV-LED illuminant (Uvata Precision Optoelectronics Co., Ltd): 365nm (Mononuclear, Quad), 385nm (Mononuclear).

Preparation of Printing Ink

Ink paste was prepared by mixing and pre-dispersing binder and pigment, and then grinding in a high-speed grinder to achieve adequate wetting and dispersing, finally the ink sample was made by fixing the prepolymers, photoinitiators, monomers and addictives.

Curing Rate Test

At room temperature, each ink sample was coated on a PET film respectively by using the No.3 wire bar. After the curing under UV-LED light source, the finger touch method and infrared spectroscopy were used to test and analyze the curing speed of each ink.

When using finger touch method to analyze the curing speed of the ink, the shortest time of ink completely curing was used to represent.

When using infrared spectroscopy to analyze the ink curing speed, the curing ink was tested by infrared spectrometer, and then the double bond conversion rate was calculated. The infrared spectra under 810cm-1 is the bending vibration peak on the C-H surface of C=C bond, the absorption peak intensity diminishes with increasing irradiation time [5]. The double bond conversion rate was calculated by formula (1) [6].

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

A_0 refers to the ink absorption intensity at 810cm-1 band without UV irradiation, At refers to the ink absorption intensity at 810cm-1 band after UV irradiation, Ct refers to double bond conversion rate of the ink. The more value of Ct, the faster ink curing speed is indicated under the same ultraviolet radiation energy.

Results and discussions

Effect of Prepolymer on Curing Rate of UV-LED Inkjet Ink

Prepolymer is the main composition of the ink. Prepolymer and monomers together form the basic skeleton of the ink. The main properties of the cured ink layer are determined by their degree of light polymerization. Due to limitations in viscosity of the inkjet ink, it was most appropriate to select the hyperbranched polyester acrylic to prepare ink. Different ink samples were prepared by changing monomers and fixing the other components of the ink, and cured by 365nm mononuclear LED light in 3s. Infrared double bond conversion rates were tested, the results were shown in Fig.1.

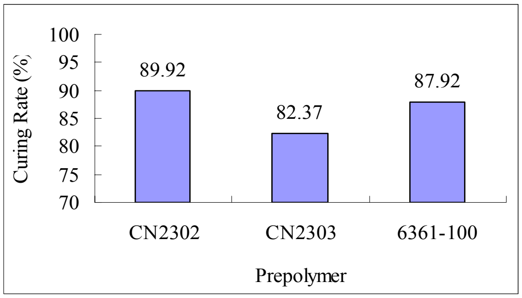

***Figure 1:** Effects of Prepolymer on Curing Rate of UV-LED Inkjet Ink*

As shown in Fig.1, effects of prepolymers on curing rate of UV-LED inkjet ink were different. The ink prepared by CN2302 had the fastest curing speed, while CN2303 the slowest. CN2302, 6361-100 and CN2303 were all the hyperbranched polyester acrylic and their functionality were 16, 8 and 6 respectively. With the increase of the functional groups of the hyperbranched polyester acrylic, the reacting activeness of photo-curing was increased, and the crossing linking density was increased, thus speeded up the curing rate of UV-LED inkjet ink.

Effect of Monomer on Curing Rate of UV-LED Inkjet Ink

Monomers are important components of the ink, not only dissolve and dilute oligomers, adjust the viscosity of the system, but also involved in the curing process, affect the light curing rate and the property of cured ink layer. Different ink samples were prepared by changing monomers, and cured by 365nm mononuclear LED light in 3s. Infrared double bond conversion rates were tested, the results were shown in Fig.2.

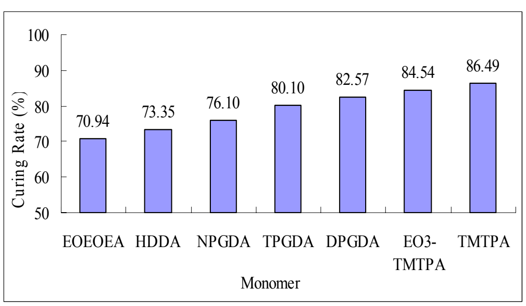

***Figure 2:** Effects of Monomer on Curing rate of UV-LED inkjet ink*

As shown in Fig.2, the curing speed of the ink accelerates with the increase of the number of functional groups of the monomer. EOEOEA prepared ink cures slowest while TMPTA cures fastest. After photopolymerization, monofunctional monomer only gets linear polymer, so the curing rate is low. Trifunctional monomer has more functional groups, greater activity, higher crosslinking density and faster curing rate. EO3-TMPTA and TMPTA are both bitrifunctional monomers. Compared with TMPTA, the former structure introduces an ethoxy group, which reduces the density of unsaturated double bonds in the monomer molecules, so the curing speed is lower than TMPTA.

Effect of Photoinitiator on Curing Rate of UV-LED Inkjet Ink

Effect of Photoinitiator Type on Curing Rate of UV-LED Inkjet Ink

Photoinitiator is the key component of the light curing system, it is related to weather the system can cause cross-linking polymerization of prepolymer and reactive diluents, so it plays a decisive role in curing speed of ink. The pigment contained in the ink forming the competition with the UV-absorbing of photoinitiator, so as to reduce the curing rate of ink, but there is a certain transmission area in UV spectral range of most pigments, namely pigment in the ultraviolet absorb weaker bands, which calls "transmitting window", selecting the photoinitiator which has high light absorption within the transmitting window of pigment can effectively improve the cure speed of ink. The transmitting window in UV spectrum region (200-400nm) of chosen pigment was in 355-365nm nearby, the spectral absorption peak of the photoinitiators were shown in table 1. Ink samples were prepared by changing the type of photoinitiator, and LED light source of 365 nm mononuclear was used to cure the inks for 3s, then infrared double bond conversion rates were tested, the results were shown in Fig.3.

Table 1: Spectral Absorption Peak of Photoinitiator

Photoinitiator	Spectral Absorption Peak (nm)	Photoinitiator	Spectral Absorption Peak (nm)
ITX	257, 382	907	232, 307
819	370, 405	369	233, 324
TPO	269, 298 379, 393		

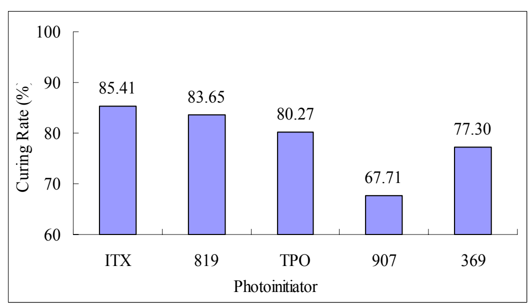

***Figure 3:** Effects of photoinitiator on curing rate of UV-LED inkjet ink*

As shown in Figure 3, inks with different photoinitiators have different curing speed, among them ITX has the highest curing speed, while TPO is the lowest. According to the Beer-Lambert Law, the UV absorption intensity of photoinitiator is directly proportional to the molar extinction coefficient. As the UV-LED light source is emitted only a single wavelength of UV light, different photoinitiators have different efficiency of the light-absorbing and different active substance quantum yield in the spectral range of UV-LED light source, so each photoinitiator leads to different curing speed.

There are absorption peaks near the transmitting window of pigment about ITX, 819 and TPO, they have high molar absorption and the absorption wavelength is close to the radiation wavelength of light source, so their curing speed is fast. ITX has photolysis products of α-amine alkyl radicals with high initiation activity, so it has the highest curing speed. The photolysis products of 819 and TPO are trimethyl benzoyl radicals and diphenyl phosphino acyloxy radicals, and 819 has one more trimethyl benzoyl radical than TPO, so it has the higher curing speed than TPO. 369 and 907 have low absorption of ultraviolet light in the transmitting window of pigment, and have low absorption of 365nm radiation wavelength, so their curing speed is low. In addition, 369 has higher molar absorption coefficient of 365nm UV-light than 907, thus speeded up the curing speed.

Effect of Photoinitiator Content on Curing Rate of UV-LED Inkjet Ink

Two groups of compound photoinitiators ITX+ 907, ITX + 327 with the proportion of 1:1 were chosen. Under the condition of the fixed other ink components, ink samples were prepared by changing photoinitiator content. LED light source of 365 nm mononuclear was used to cure the inks, and finger touch method was used to test its curing rate. The test result was shown in figure 4.

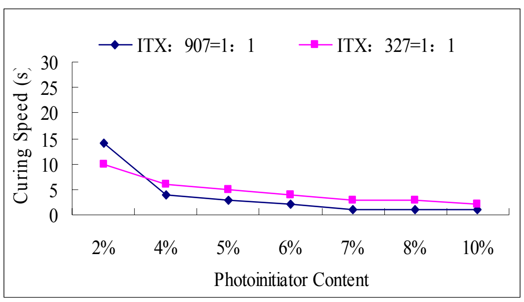

Figure 4: *Effect of Photoinitiator Content on Curing Speed of UV-LED Inkjet Ink*

As shown in Figure 4, the ink curing velocity speeded up quickly along with the increase of photoinitiator content when photoinitiator content within 2-7%, while it speeded up slowly with the increase of photoinitiator content when photoinitiator content within 7-10%. Under certain UV-LED energy radiation, ink absorbed less UV energy and produced only a small amount of free radicals when the photoinitiator content was low, and the curing speed was slow. When photoinitiator content increased within a certain range, the absorption of ultraviolet energy was increased, and more free radicals were produced to improve the curing speed. However, because of the weak of light emission intensity, when the photoinitiator content increased, the ink film surface absorbed more ultraviolet light, which resulted in the decrease of luminous flux of reaching the inside of ink film. Because the number of the free radicals formed in the depth within the coating layer of the ink film was proportional to the photoinitiator content and the light intensity in the region [7], the absorption of UV light energy inside the ink membrane is stabilized, and ink curing rate changed little, although photoinitiator agent content was high in the region.

Effect of Composite Photoinitiator on Curing Rate of UV-LED Inkjet Ink

In order to improve the curing speed of ink, ITX, 819, and TPO were chosen to design co-photoinitiator by formulation experiment. Seven kinds of the formulas with different photoinitiators should be designed to prepare the ink samples, after being coated and cured, infrared spectroscopy is used to analyze the double bond conversion rate of the ink. Formula experiments and results were shown in Table 2.

Table 2: Formula Experiments and Results

Item	X1(ITX)	X2(819)	X3(TPO)	Conversion Rate (100%)
1	1	0	0	68.78
2	0	1	0	69.35
3	0	0	1	61.88
4	1/2	1/2	0	82.45
5	1/2	0	1/2	69.92
6	0	1/2	1/2	75.51
7	1/3	1/3	1/3	72.25

The regression equation between standardized variables and test indicators was shown in Equation (2).

$$\hat{y} = \sum_{i=1}^{3} b_i x_i + \sum_{i<j} b_{ij} x_i x_j + b_{123} x_1 x_2 x_3 \qquad (2)$$

The double bond conversion rate of Table (2) was taken into the formula to get the regression coefficient, and then the coefficient was taken into the regression equation to get the regression equation between curing speed and variables, which was shown as Formula (3).

$$y = 68.78x_1 + 69.35x_2 + 61.88x_3 + 53.54x_1x_2 + 18.36x_1x_3 + 39.58x_2x_3 - 183.78x_1x_2x_3 \qquad (3)$$

The greater value of regression equation, the faster the curing speed of the ink is. When X1 = 0.4946, X2 = 0.5054, X3 = 0, the maximum value was 82.45 in the regression equation. After the analysis of data, under the experimental conditions, the optimal mass ratio of composite photoinitiator of ITX: 819 was 1:1, it can obtain the highest curing speed and now the double bond conversion rate reached 75.51%.

Effect of Illuminant on Curing Rate of UV-LED Inkjet Ink

Because of the limitation of semiconductor material component, UV-LED illuminant emitted a monochromatic light with narrow wave peak band. In order to investigate the effect on ink curing rate of UV-LED illuminant with different wavelength and energy, different photoinitiators were used to prepare ink and then cured under different illuminants, finger touch method was used to test the curing speed, the results are shown in Figure 5.

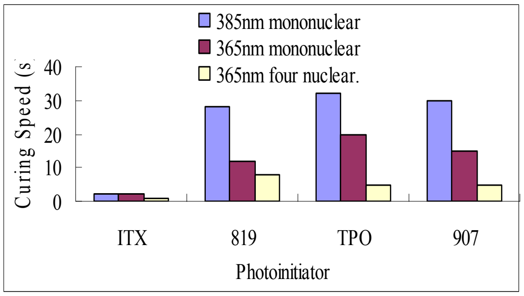

Figure 5: *Curing Rate of Different UV-LED Light Sources*

As shown in Figure 5, the irradiation power and ultraviolet wavelength of the illuminant have different effectiveness on the curing speed of UV-LED jet ink. Curing under conditions with the same irradiation power but different ultraviolet wavelengths, inks cured by UV-LED light source with wavelength 365nm has higher curing efficiency than the ones with wavelength 385nm. This is because the wavelength of the radiation source 365nm light near the transmitting window of the pigment, which can contribute to the UV energy absorption of photoinitiator, thus the curing speed is faster. Curing under conditions with the same wavelength of ultraviolet but different power of radiation, light intensity of four-nuclear UV-LED illuminant is higher than mononuclear UV-LED illuminant, and the photoinitiator can absorb more ultraviolet light at the same irradiation time under four-nuclear UV-LED illuminant, so the ink curing speed can be improved significantly. In addition, the ink prepared with photoinitiator ITX has the fastest curing speed when cured by 365nm four-nuclear UV-LED illuminant, is means that the correctly match of photoinitiator and illuminant can effectively improve the ink curing speed.

Conclusion

By above analyses, such conclusions can be obtained under certain experiment conditions.

1) As the increase of the functional groups of the hyperbranched polyester acrylic, curing rate of UV-LED inkjet ink speeds up and ink prepared with CN2302 has the highest curing velocity.

2) As the quantity of the functional groups of the monomer increases, curing rate of UV-LED inkjet ink speeds up and ink prepared with TMPTA that has three functional groups has the highest curing velocity.

3) It can improve the curing speed of UV-LED inkjet ink to match spectrum absorption peak of photoinitiator, spectral radiation peak and pigment transparent window and to use high power light. Ink prepared with ITX and lighted with 365 nm quad-core LED light source has best curing speed.

4) The UV-LED inkjet ink with composite photoinitiator has a faster curing speed than the ink with single photoinitiator. When the mass ratio of composite photoinitiators of ITX and 819 is 1:1, the curing speed is the highest.

5) The curing speed of UV-LED inkjet ink increases along with the increase of the photoinitiator content, but when the photoinitiator content is more than 7%, increasing photoinitiator content has little effect on the improvement of the ink curing speed.

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