The Study of the Influence of Photoinitiators on Curing Rate in UV System under Different Oxygen Atmosphere

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Abstract

The UV system contains prepolymer, monomer and photo-initiator has been broadly used in printing area. UV-curable inkjet ink with its environmental protection, energy-saving, good printing quality and high efficiency has become the most concerned topic and has a good development prospects. The use of UV ink-jet printing ink in ink-jet digital printing is the main development trend of digital printing currently and a period of time in future. Curing rate is one of the most important performance parameters of the UV system which is greatly affected by prepolymer, monomer and photo-initiator, besides that, the oxygen atmosphere is another principal element. In order to investigate the influence of different oxygen atmosphere on the curing reaction, we designed and made a UV curing device with varied degree of oxygen atmosphere to study the effect of photo-initiator species and content on the systems curing rate under different oxygen atmosphere condition.

Keywords: *Photo-initiator; UV system; Curing rate; Oxygen atmosphere*

Introduction

UV ink, i.e. ultraviolet curing ink, with irradiation of 200 ~ 450nm ultraviolet, the photo-initiator absorbs radiation and forms free radicals or cations, polymerization, cross-linking and grafting reaction occurs between monomers and pre-polymers, and solidified into a three-dimensional network structure in a short time. It has many advantages such as fast-drying, high printing production efficiency, low energy consumption in low temperature curing, high gloss, good resistance, no solvent evaporation, environmental protection, etc. As a main trend of ink technology, it has been more widely used in the printing industry [1].

Photo-initiator is the key component of UV ink system; it relates to whether the monomer and pre-polymer can crosslinking after the ink system receive light radiation energy and generate initiators. Generally, curing is carried out in the air, so oxygen inhibition exists in almost all of the UV curing reactions. Oxygen inhibition consumes more energy, and extends curing time. So it is very important to study the initiator impact on curing speed of UV systems under different oxygen atmosphere.

Experiments

Experimental materials

Pre-polymer: acrylate pre-polymer 6325-100

Monomer: Hexanediol diacrylate(HDDA),2-(2-Ethoxyethoxy) Ethylacrylate (EOEOEA);

Photo initiator: 1-hydroxyl-ring has base-a ketone phenyl (184), Trimethyl benzoyl diphenyl phosphine oxide (TPO), Benzophenone (BP), 2-isopropyl thioxanthone（ITX）

Other promoters: 2-Ethylhexyl 4-dimethylaminobenzoate (EHA), surfactant, flow agent, dispersant etc.

Equipment

Magnetism Msier (China), Shimadzu FTIR-8400 Fourier transform infrared spectrometer（Japan）, Vacuum UV curing device (China).

Samples preparation

Design a UV system, prepare samples, and mix well by Magnetism Msier. Samples number is shown in Table 1. Ink component: 40% pre-polymer, 50%monomer, 5% active amine.

Table1. Samples number

Sample	1	2	3	4	5	6	7	8
Photo-initiator	BP	TPO	ITX	184	ITX	ITX	ITX	ITX
Contents (%)	5	5	5	5	1	4	6	10

Coating the samples on the transparent film by certain thickness, curing by UV radiation under different oxygen atmosphere, tests their infrared absorption spectra, and calculates double bond conversion according to equation 1

Test method of double bond conversion rate

Using infrared spectroscopy, C = C double bond conversion is tracked with the illumination time to obtain polymerization conversion rate curve (generally, IR peaks are the C = C double bond and bending vibration peak out of C-H plane, respectively near by 810cm^{-1} and1410cm^{-1}, C = C double bond located near1630cm-1 is the stretching vibration peak)[2].

The width and position of C = C bond absorption peak will not change in polymerization process; the baseline of C = C bond independent spectral bands can be measured accurately; absorption strength of monomer is corresponding with absorption spectrum of monomers' C = C bond, which decreases with irradiation.

In order to obtain the correct determination of thin films, an internal standard is required and a special spectrum is chosen as a reference .The intensity of this spectrum does not change with the monomer double bond conversion i.e. remove samples from radiation exposure at different times or with different energy radiation and tesr the infrared spectrum. In this paper, double bond conversion rate can be calculated as follows:

$$C_r = \frac{A_0 - A_x}{A_0} \times 100\% \qquad (1)$$

$A_0$is the spectrum absorption strength ratio of 810cm^{-1} and 1730cm^{-1} without the ultraviolet radiation, Axis spectrum absorption strength ratio of 810cm^{-1} and 1730cm^{-1} with the ultraviolet radiation under a certain time t . Cr is double bond conversion rate under conditions in the corresponding [3].

In order to show the curing reaction with the change, the reaction rate in the time Δt is shown by relative reaction rate Rp, relative reaction rate can be calculated by the following formula:

$$R_P = \frac{\Delta[M]}{\Delta t} = [M]_0 \frac{\Delta C_r}{\Delta t} = [M]_0 \frac{\partial C_r}{\partial t} \qquad (2)$$

$[M_0]$ is the initial concentration of polymerization monomer. t is the ultraviolet radiation time .The rate shown by the relative reaction rate is because $[M_0]$ is only the initial polymerization monomer concentration, while the double bond conversion rate is relative to the terms of the ink system.

From the above formula, reaction rate and conversion rate is proportional to the double bond conversion rate.

Test method of oxygen inhibition

The stable state of oxygen is triplet state, oxygen itself is relatively stable, but in the UV curing oxygen and curing surface may quenching initiator excited state and chain growth radicals' clearing reaction etc. From oxygen inhibition mechanism analysis we can know that there are the following two aspects about inhibiting oxygen inhibition role: on the one hand reducing the oxygen in the curing system, which is the most important issue; on the other hand improving the curing formulations, improving curing rates, reducing the curing time and reducing oxygen diffusion to the coating surface also purpose to inhibit the effect of oxygen inhibitor [4]. Based on the view, this paper designs the vacuum curing box as shown in Figure 1 .As shown, ink samples can be placed in the curing box to curing in different oxygen concentrations.

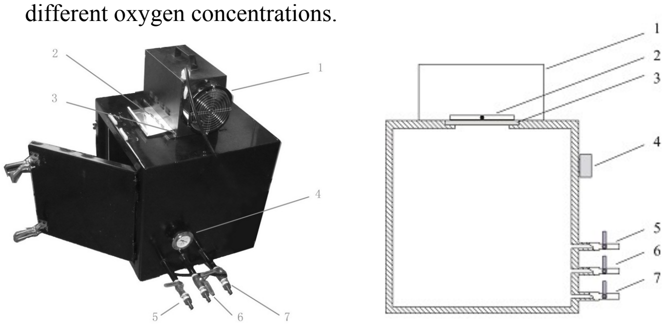

Fig.1 Structure of the vacuum UV curing device

1 UV lamp（100W/cm optional）; 2 Manual shading plate; 3 Quartz plate; 4 Vacuum Gauge; 5 Vacuum pump interface; 6 Oxygen intake; 7 Exhaust port

Results and Discussion

Influence of the variety of photo-initiator on the curing rate of UV system under different oxygen content

Photo-initiator absorbs UV energy, produces free radicals, and then generates polymerization reaction. It is organic compounds with special perssad which stimulate light-cured resin to be crosslink. in the photochemical reaction, with excitation of light the initiator absorbs photons and becomes very active, it produces free radicals, transfers energy to the polymer, occurs chain reaction, change the linear resin to network structure, so that curing the ink into a tough film [5].

UV system has prepared by mixed EHA with photo-initiator BP/ TPO/ ITX/184 respectively. Use the vacuum curing box with 100 W/cm high-pressure mercury lamp, at room temperature, irradiation distance is 12 cm, and exposure them in different oxygen concentration for 10 s, to investigate the curing effect of different initiator and test samples' double bond conversion rate, test results has shown in figure 2.

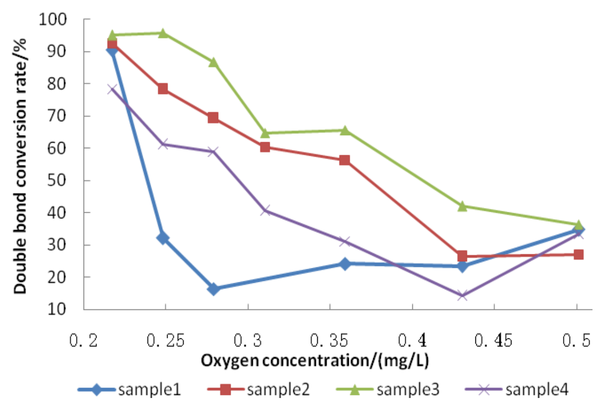

Fig.2 Double bond conversion rate of sample1~sample4 vs. different oxygen concentration

Fig.2 shows that in the extremely low oxygen concentration, all of four samples has high double bond conversion rate, with the increase of oxygen conversion double bond conversion rate has decline sharply, this shows that oxygen has significant inhibitory effect to UV cure, as oxygen can cause the quenching of initiators' excited state and scavenging the propagated free radicals etc. It has inhibition to polymerization, the higher the oxygen content, the stronger the inhibition.

Whether the photo-initiator matches the UV light radiation bands has directly impact on the speed of curing reaction. As ITX and TPO's absorption peak near by the radiation peak of the ultraviolet light, so they have the highest cure rate. In addition, because ITX and BP are Ⅱ types photo-initiators, so that in cooperation with the H donor, the tertiary amine is H donor and oxygen polymerization inhibitors as well. Select EHA, N is connected with the benzene ring, and increase the electron density on N, and will result in necleophilic reaction; the other side of the benzene ring connected with ester, the extended conjugated system is easy to loss hydrogen, so it has good effect to inhibit the oxygen inhibition [4]

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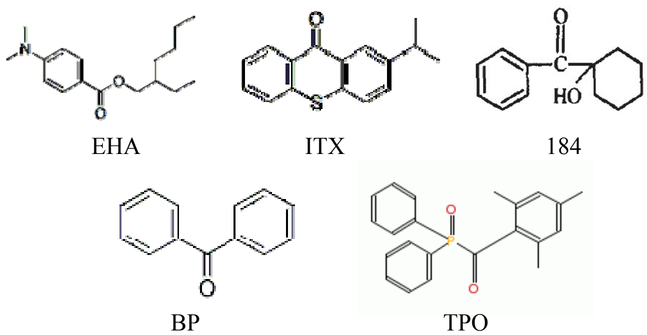

Fig.3 the structure of initiator and activity amine

There's special conjugate structure which consist of three six-membered ring in ITX molecules, S atoms can be approximated as in the same plane, can participate in conjugation, reduce the electronic transition energy, and the UV absorption peak has blue shift, with absorption enhancement, there is a strong absorption near 380nm, after excited by the light and then occurs hydrogen abstraction reaction, the free radicals cause photo-polymerization, the quantum yield is higher, and cure rate is higher too. So the double bond conversion rate of ITX system is significantly higher than TPO and 184, but because of BP's photo-initiation performance is very weak and not matches with the output wavelength light of mercury lamp, so the double bond conversion rate is relatively lower.

Photoinitiator content's influence on the curing speed of UV systems under different oxygen contents

Choose ITX/EHA initiator system which has trigger efficiency and better inhibit effect, double bond conversion rate changes with different initiator concentrations under the different oxygen concentrations. Test results are shown in Figure 4.

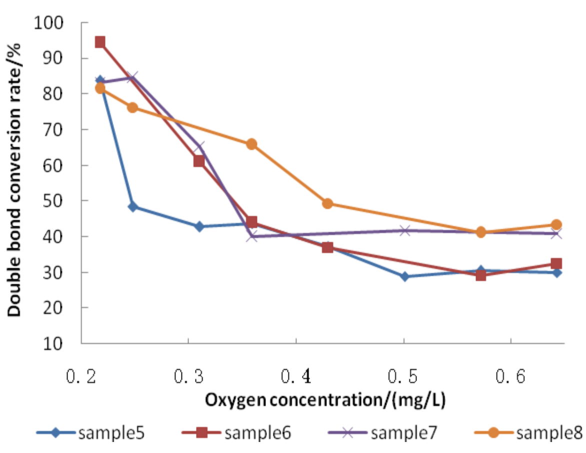

Fig.4 Double bond conversion rate of sample5~sample8 vs. different oxygen concentration

From Figure 4, in the case of low oxygen concentration, double bond conversion rates of samples are very high, with the oxygen content increases, the double bond conversion rates show a downward trend, which has the same analysis of Figure 3. Initiator content is less than 10%, the higher the initiator concentration, the slower the decline, the higher double bond conversion rate, the higher curing rate, this is because:

$$R_p = k_p[M](\phi \varepsilon I_0[s]/k_t)^{1/2} \quad (3)$$

Among them, R_p—the light polymerization reaction rate, K_p—chain growth rate constant, ϕ —the quantum yield of free radicals, K_t— the chain termination rate constant,[M]—monomer concentration, [S] --the concentration of photoinitiator, ε--molar extinction coefficient of photoinitiator , I_0 --light intensity.

When initiator efficiency and decomposed primary free radicals constant are fixed, photonitiator concentration increases, light trigger rate increases, that is to say, curing speed increases.

When Initiator concentration is very low, the curing rate is slow because a small amount of radicals which generates by the low concentration initiator has mainly consumed by oxygen, so that curing reaction is difficult to occur. When the initiator concentration is a little higher, initiator light density will increases in a certain range. This can make the absorption of light energy increase, so the chain initiation rate increases [5].

Therefore, an appropriate increase of photoinitiator concentration can reduce oxygen inhibition effects on ink curing.

Conclusion

The varieties of photoinitiator have a great impact on the curing rate of UV systems as well as the impact of oxygen content. Photoinitiator system of Ⅱ type composed by ITX and EHA has high double bond conversion rate and faster cure rate.

In vary low oxygen content, double bond conversion rate is high, with the oxygen content increases, the double bond conversion rate was significantly decreased.

Photoinitiator content has a great impact on the curing speed of UV systems. Initiator content less than 10%, the higher the initiator concentration, the higher the double bond conversion rate. An appropriate increase of photoinitiator concentration can reduce oxygen inhibition effects on ink curing.

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