Effect of Tertiary Amine on the Curing Rate of UV-curable Ink

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Abstract

Curing rate is one of the most important performances of UV-curable ink, while the tertiary amine has a certain impact on the curing rate. UV-curable flexo ink was used as the research object. Ink samples with different type of tertiary amine and photoinitiator were prepared. In order to study the impact of tertiary amine and its matching with photoinitiator on the ink's curing rate and the oxygen inhibition effect, the double bond conversion rate of the samples were tested at atmosphere of different oxygen concentrations. In addition, ink samples with different ratio between tertiary amine and photoinitiator were made, and the double bond conversion rate was tested to study the influence of ratio between tertiary amine and photoinitiator on the curing rate. The result shows that tertiary amine has a significant restrain on the oxygen inhibition; tertiary amine's structure has a great effect on both the UV ink curing rate and the oxygen inhibition. Norrish type II photoinitiator should match with the appropriate tertiary amine in a suitable ratio in order to achieve a higher curing rate.

Key words: Tertiary amine; UV-curable ink; Photoinitiator; Curing rate

1. Introduction

UV-curable ink with fast curing speed, no pollution and high print quality, has become more and more widely used in the printing industry [1]. Curing rate as one of the most important properties of UV-curable ink has a direct impact on the printing speed. The photoinitiator forms free radicals or cationic by UV radiation to initiate polymerization, cross-linking and grafting reaction of monomer and oligomer [2]. UV-curable ink becomes a polymer of three-dimensional structure in a very short time. Photoinitiators can be divided into Norrish type I and Norrish type II, while the Norrish type II photoinitiator must be used with hydrogen donor (which is usually tertiary amine) containing reactive hydrogen by Norrish type II reaction to form free radicals [3]. In the reaction, the tertiary amine can also consume a certain amount of oxygen to prevent oxygen quenching effect on photoinitiator, so the oxygen inhibition is well restrained [4]. Therefore, the impact of tertiary amine on ink's curing rate cannot be ignored. During the preparation of UV-curable ink, it's very helpful for increasing the curing rate by selecting the appropriate tertiary amine.

2. Experiment

2.1 Materials

Oligomers: 6311-100, 6325-100, EB450, EB812;

Monomers: EOEOEA, HDDA, NPGDA, TPGDA, DPGDA, TMPTA;
Pigment: Ciba RT-355-D;
Photoinitiators: ITX, DETX, BP, 907;
Tertiary amines: EHA, EDB.

2.2 Equipment

Grinding equipment: GJ-2S high-speed grinding mill (China);
Curing equipment: Fusion Light Hammer 6 (USA);
Testing equipment: Shimadzu FTIR-8400 Fourier transform infrared spectrometer (Japan).

2.3 Experimental Methods

UV-curable flexo ink was used as the research object for studying the influence of tertiary amine on the curing rate of UV-curable ink because of its rapid development in the industry.

2.3.1 Preparation

Preparation of UV flexo ink was separated into two parts. First, mixture of pigment , oligomers and monomers was grinded by the high-speed mill to prepare well-dispersed primary ink. Then the diluted oligomers , monomers , photoinitiators and tertiary amines were added to the primary ink to obtain inks.

2.3.2 Measurement of curing rate

The ink sample was exposed to UV radiation for a certain time. Curing rate was determined by the double bond conversion rate calculated according to the infrared spectrum absorption intensity. As shown in the following formula：

$$C_r = \frac{A_0 - A_x}{A_0} \times 100\%$$

A_0 is the ratio of intensity at 810cm^{-1} and 1730cm^{-1} absorption bands of ink without UV radiation； A_x is the ratio of intensity at 810cm^{-1} and 1730cm^{-1} absorption bands of ink after a certain time of UV radiation ; C_r represents the double bond conversion rate of ink under the condition [5].

2.3.3 Measurement of oxygen inhibition

A vacuum UV curing device was made to inspect the oxygen inhibition. As shown in Fig.1, by controlling the vacuum level and the oxygen flow of the device, ink samples were irradiated at atmosphere of different oxygen concentration, and then tested the curing rate of the samples.

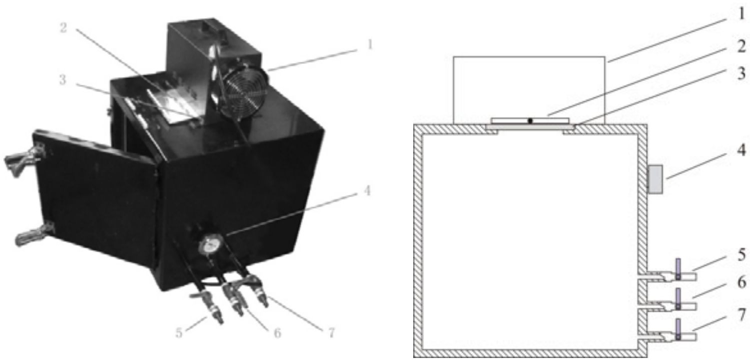


Fig. 1. Structure of the vacuum UV curing device

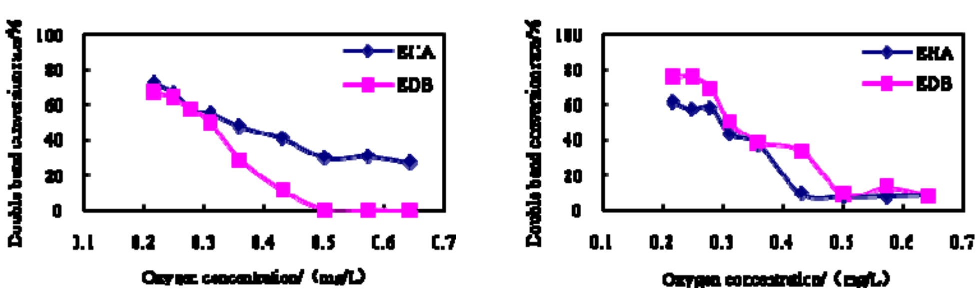
1. UV lamp (100W/cm, 200W/cm optional); 2.Manual shading plate; 3.Quartz plate; 4. Vacuum Gauge; 5.Vacuum pump interface; 6.Oxygen intake; 7.Exhaust port (also used as gas inlet)

3. Results and discussion

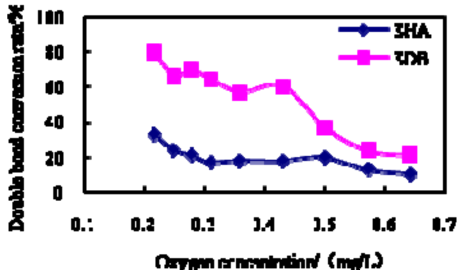
3.1 Impact of tertiary amine type on curing rate

Norrish type II photoinitiator must be used with hydrogen donor (which is usually called activating agent) containing reactive hydrogen, by Norrish type II reaction to form free radicals for initiating the polymerization between oligomer and monomer in the ink. Tertiary amine is one kind of very reactive hydrogen donors, often used in conjunction with Norrish type II photoinitiator [6]. Different type of tertiary amine has different reactivity, which has a certain impact on the curing rate of UV-curable ink.

Without changing other compounds，UV-curable flexo magenta ink samples were prepared by using two tertiary amine 2–Ethylhexyl–4-dimethylaminobenzoate (EHA) and Ethyl-4-dimethylaminobenzoate (EDB) respectively matching with three Norrish type II photoinitiator Benzophenone (BP), 2-Isopropylthioxanthone (ITX), Diethylthioxanthone (DETX). At room temperature, ink samples were exposed to the 100W/cm UV lamp at an irradiation distance of 50cm for 10 seconds in the vacuum device under different oxygen concentrations. Curing rate, which is the double bond conversion rate, was tested to study the effect of different matching of tertiary amine and Norrish type II photoinitiator on the curing performance (Fig.2).



(a) ITX (b) DETX



(c) BP

Fig.2. Impact of tertiary amine type on the curing rate of UV-curable ink

As can be seen from Fig.2, using different type of tertiary amine in the UV ink preparation can obtain different curing rate and combination with different photoinitiator, curing effect is also different. In Fig.2 (a), for ITX, used with EHA can obtain faster ink curing rate than EDB, while in (b) & (c), for DETX & BP, curing rate was greater when matched with EDB. This is caused by the structure of the compound initiated by the reaction between photoinitiator in the excited triplet state and tertiary amine. Most Norrish type II photoinitiators are aromatic ketones, can react with tertiary amine to form excited state compound by UV irradiation. Then electron transfer occurs, one of the N lone pair electrons transfers to the carbonyl, carbonyl radicals and very lively amine positive ions are formed. The latter due to increased acidity soon lost their protons, turn into very reactive alkyl amine radicals. Carbonyl radicals mainly disappear from radical coupling or disproportionation reaction, while alkyl amine free radicals are to initiate polymerization [4]. After photoinitiator DETX and BP crossing to the excited triplet state by UV excitation, the conjugation effect is greater when reacting with EDB than EHA in formation of excited state compound. So the α-H of EDB is more reactive and the electron transfer reaction rate is quicker and either is curing rate of the prepared ink. Similarly, the conjugation effect is greater when ITX is reacting with EHA than EDB, and so is the curing rate. Norrish type II photoinitiator should be added to the UV ink with tertiary amine of appropriate structure, so that the electron transfer rate of the excited state compound created by reaction between photoinitiator and tertiary amine will be higher, which leads to better curing rate.

3.2 Impact of tertiary amine on oxygen inhibition

Without changing other compounds，UV-curable flexo magenta ink samples were prepared by adding Norrish type I photoinitiator 907 without tertiary amine, with EHA and EDB. At room temperature, ink samples were exposed to the 100W/cm UV lamp at an irradiation distance of 50cm for 10 seconds in the vacuum device under different oxygen concentrations. Double bond conversion rate was tested to study the effect of tertiary amine on oxygen inhibition (Fig.3).

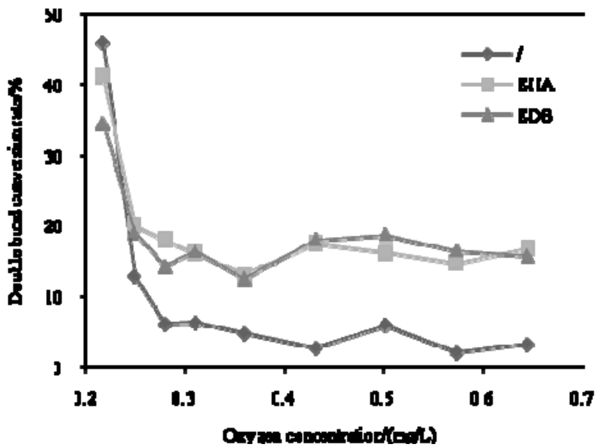


Fig.3. Impact of tertiary amine on oxygen inhibition of UV-curable ink

In Fig.3, with the increasing of oxygen concentration, the double bond conversion rate of ink sample with tertiary amine was significantly higher of than the one without tertiary amine. 907 is a Norrish type I photoinitiator, can generate free radicals I from self-cracking by UV irradiation, even after the addition of different tertiary amines, when the oxygen concentration was low, less oxygen dissolved in the surface and inside of the ink layer, the oxygen inhibition effect was little. There was not a big difference in the double bond conversion rate. However, when oxygen concentration continue to raise, the double bond conversion rate of the sample without tertiary amine fell rapidly, while the other two remained a relatively high rate, which indicated that tertiary amine has a great influence on oxygen inhibition. Because the photochemical intramolecular abstraction of α-H on tertiary amine formed alkyl radicals, which can easily react with oxygen, at the same time of consuming oxygen, it created new active free radicals preventing oxygen quenching on photoinitiator to improve the curing rate.

Fig.2 also illustrates tertiary amines restrained the oxygen inhibition; different tertiary amine had different impact on oxygen inhibition. Along with the increase of oxygen concentration, double bond conversion rate of ink sample with EHA was smaller than with EDB, indicating EHA has greater impact on oxygen inhibition, and explains that the structure of tertiary amine affects the restraining of oxygen inhibition [7]. The more reactive the α-H of tertiary amine is, the easier to form alkyl amine radicals, the more consumption of oxygen and the better effect of restraining oxygen inhibition [8]. As far as these two kinds of tertiary amines are concerned, ester group is attached to the other side of the benzene ring, as EHA's ester group is larger than EDB, causing a bigger loss of hydrogen in the conjugated system, the α-H is more reactive, so EHA's inhibition on oxygen polymerization was better, corresponding higher double bond conversion rate, so as to higher curing rate.

3.3 Tertiary amine's content on the curing rate

Fixing content of other ingredients , UV-curable flexo magenta ink samples were made with initiating system of ITX/EHA by changing their ratio when the total content remained at 8%. Ink samples were exposed to UV radiation of 86mJ/cm^2. Double bond conversion rate was tested to study the effect of photoinitiator/tertiary amine ratio on curing rate (Fig.4).

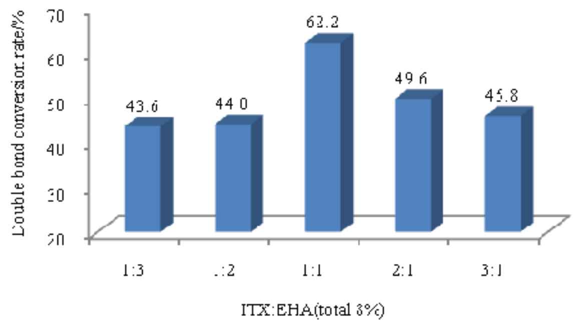


Fig.4. ITX/EHA ratio on the double bond conversion rate of UV-curable flexo ink

From Fig.4, along with the increase of tertiary amine proportion, ink's double bond conversion rate increased, after reaching the highest point, the conversion rate declined despite of the increase ratio. When at the ITX/EHA ratio of 1: 1, conversion rate reached the maximum, that is, the highest curing rate. It indicates that too much or too little tertiary amine are all negative to UV curing: too little that less main reactive alkyl amine radicals were generated for initiating the ink polymerization, in addition, not give full benefit on the restraining of oxygen inhibition; too much that the reactive radicals generated per volume unit was excessive, and photochemical reaction intermediates with ITX has also increased, resulting in decreasing polymerization rate for the inner extinction effect. Therefore, Norrish type II photoinitiator and tertiary amine must have an appropriate ratio, in order to gain high curing rate of UV ink.

4. Conclusion

Based on the experiments, the following conclusions were obtained:

(1) Norrish type II photoinitiator should be added to the UV ink with tertiary amine of appropriate structure, so that the electron transfer rate of excited state compound that created by reaction between photoinitiator and tertiary amine will be higher. Combination of ITX/EHA, DETX/EDB and BP/EDB can achieve faster curing rate.

(2) Tertiary amine has a great influence on oxygen inhibition. The more reactive of the α-H on tertiary amine results in better restraining effect on oxygen inhibition. EHA's restraining impact was greater than EDB's in this experiment.

(3) Norrish type II photoinitiator and tertiary amine must have an appropriate ratio to gain high curing rate. When ITX/EHA ratio was 1:1, UV-curable ink had the highest curing rate.

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