Study on the curing performance of UV-curable inkjet ink

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Abstract

Photo-initiator and monomer seriously affect the curing performance of UV-curable inkjet ink. According to study the effects of the different photo-initiators on the curing rate of UV-curable four-color inkjet ink, the formulation experiment was made by three photo-initiators. The four-color inks could obtain the optimum proportions. Through studying on the curing rate and viscosity of inks prepared by different monomers, the mixed monomer which was made up of EOEOEA、TPGDA and TMPTA was designed in this paper, the optimum proportion could be obtain by the way of formulation experiment is EOEOEA:TPGDA:TMPTA＝5.5:2:1.5。

Keywords

UV-curable inkjet ink, curing rate, the way of formulation experiment.

1. Summary

UV-curable inkjet ink with energy-saving, environmentally friendly and high efficiency has become the most concerned new ink and has the tremendous prospects for development[1]. As the important components of UV-curable inkjet ink, photo-initiator and monomer seriously affect the curing rate of UV-curable inkjet ink. Photo-initiator can generate free radicals by the specific wavelength of UV and initiate polymerization reaction. Monomer participates in light-curing process and affects curing kinetics, the degree of polymerization and the physical property of the generating polymer. In addition, because of the higher viscosity of pre-polymers, the system needs monomers to decrease the viscosity. Therefore, the choices of photo-initiator and monomer are the important parts of the designed formulation of UV-curable inkjet ink.

The curing rates of inks prepared by six photo-initiators were tested, and the effects of photo-initiator on curing performance of UV-curable four-color inkjet ink were separately studied. In order to improve the curing performance of UV-curable four-color inkjet ink, the three photo-initiators were mixed and the optimum proportion of the three photo-initiators was confirmed by the way of formulation experiment. Through studying on the curing rate and viscosity of inks prepared by different monomers, the mixed monomer which was made up of EOEOEA、TPGDA and TMPTA was designed in this paper, the optimum proportion could be obtained by the way of formulation experiment.

2. Experiment

2.1 Raw materials

Pre-polymer: the type of PU CN2300;
Monomer: EOEOEA, TPGDA, TMPTA;
Pigment: Irgalite Blue Glvo,Ciba;
Photo-initiator: TPO, 184, 651, 907, 1173, ITX;
Dispersant: CH-13, San zheng, Shang hai.

2.2 Apparatuses

YM-I milling equipment;
5＃ viscosity cup;
UV curing machine, FUSION, American;
FTIR-8400，shimadzu, Japan;
Laser particle sizer, 3500, Microtrac;
Surfance tension apparatus, K100, Kruss;
Conductivity apparatus, DDS-307.

2.3 The preparation of linking substances and inks

The linking substances were prepared by mixing pre-polymer, monomers and photo-initiators and were agitated evenly.

The inks were prepared by mixing linking substances, pigment and dispersant and were grinded by using the YM-I milling equipment.

2.4 The testing method of curing rate

The monomers which participate in the reaction of light-curing contain the unsaturated double bond or epoxy group. Because all this groups have characteristic absorption bands in infrared spectrum, the groups will gradually disappear with the progress of the curing reaction. Accordingly, the intensities of absorption bands also decrease gradually. So the extent of curing reaction is characterized by utilizing the change of the intensities of absorption bands. The important substances in the system of UV-curable inkjet ink is the type of acrylate, therefore, the wave numbers of the common bands are $810cm^{-1}$ in which the double bond has twisting vibration and $1630cm^{-1}$ in which the double bond has stretching vibration. The extent of curing reaction is demonstrated by testing the infrared absorptions of samples in different conditions and utilizing the change of the intensity of absorption band in $810cm^{-1}$. The curing rate can be calculated by the formula (1) [2]

$$\text{Curing rate} = (A_0 - A_t)/ A_0 \times 100\% \quad (1)$$

In this formula, A_0 represents the intensity of absorption band in $810cm^{-1}$ before curing reaction; A_t represents the intensity of absorption bands in $810cm^{-1}$ after the t time in curing reaction.

3 Results and discussion

3.1 The effect of photo-initiator on the curing performance of UV-curable four-color inkjet ink

3.1.1 The effect of different photo-initiator on the curing performance of UV-curable four-color inkjet ink

Take cyan ink as an example, the curing rates of inks which were respectively prepared with photo-initiators TPO, 184, 651, 907, 1173, ITX were tested. The tested results are showed in figure 1 below.

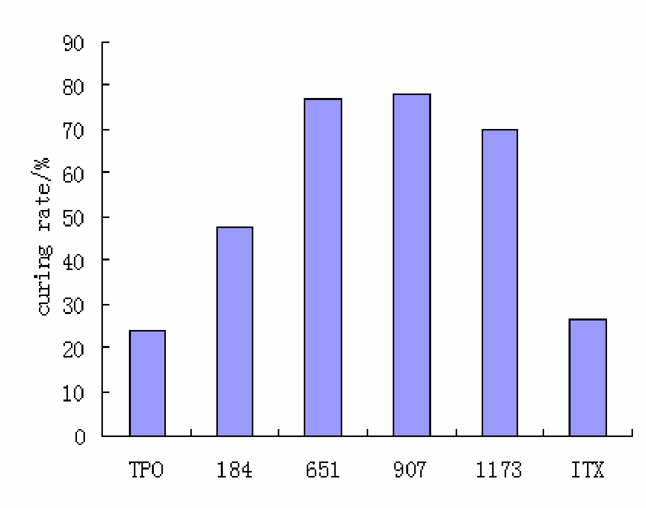

Figure1. The effect of different photo-initiator on curing rate of UV inkjet ink

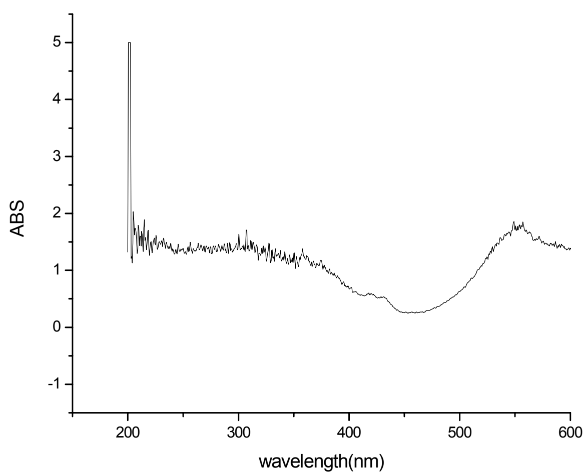

Figure2. The absorption curve of cyan pigment

Figure 1 shows that the curing rates of inks prepared by 651, 907, 1173 are higher than others. These results are because of the close relations of the absorption curve of UV spectra between photo-initiator and pigment. Most of pigments have weak part on the absorption curve of UV spectra, which is called "transmission window". With these "transmission windows", appropriate photo-initiators can be selected, whose absorption peak should be at the "transmission window" of pigment. The selection of photo-initiators is the key factor of improving the curing performance of UV- curable inkjet ink. The more the absorption peak of photo-initiator are in the effective range ("transmission window" of pigment), the stronger ability to capture ultraviolet is. Figure 2 shows that the weak absorption part of selected cyan pigment on UV spectra ("transmission window") is at the scopes between 230nm and 260nm and between 340nm and 360nm, the absorption peaks of 907 and 1173 are at 235nm and 240nm separately, and the absorption peaks of 651 are at 255nm and 345nm. All the absorption peaks of these photo-initiators are in the range of the "transmission window" of cyan pigment, so the curing rates of inks prepared with 651, 907, 1173 are high.

In addition, because the photo-initiator become effective only after absorption of UV energy, the matching between the absorption of photo-initiator and the radiation of UV energy source affects the curing velocity of UV-curable ink. The radiation peaks of UV energy source D are around 250nm, 310nm, and 380nm. And the absorption peaks of photo-initiators 907 and 651 are close to these radiation peaks, at 310 nm and 255nm. Especially, the absorption peaks of 907 are exactly same as the radiation peaks of UV energy source D. So the curing rate of ink with 907 is highest of all, and the curing rate of ink with 651 is the second one.

In vicinity of transmission window, photo-initiators TPO、184 and ITX also have absorption peaks, but their curing rates were less possibly because of less initiate efficiency.

For magenta ink, the curing rates of Inks prepared by photo-initiator TPO、907 and 1173 are much greater. For black ink, the curing rates of Inks prepared by photo-initiator TPO、184 and 1173 are much greater. For yellow ink, the curing rates of Inks prepared by photo-initiator TPO、184 and 651 are much greater.

3.1.2 The effect of the mixed Photo-initiator on UV-curable inkjet ink

According to study on the effects of different photo-initiators on UV-curable four-color inkjet ink, the photo-initiators which has high curing rate can be chose. In order to improve the curing rate of UV-curable inkjet ink, the inks prepared by the mixed photo-initiator with the way of formulation experiment, the optimum proportion can be obtained.

Take cyan ink as an example, the formulation of the mixed photo-initiator was designed by the way of formulation experiment which adopts the simple design of three components in the center of gravity[3], as shown in table1. X1, X2 and X3 are respectively supposed as the proportions of 651、907 and 1173. Adopting the simple design in the center of gravity (m=3), there are seven formulations, as shown in table1. At the same time, the table1 also shows the tested curing rates of inks prepared by formulations. As m equals to three, the expression of regressive equation is shown in equation(2).

$$y = b_1x_1 + b_2x_2 + b_2x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \tag{2}$$

Replacing the parameters in regressive equation above with the data in table1, it can get seven equations. By solving the seven equations together, the seven regression coefficients can be calculated, and then the regressive equation can be obtained, as shown in equation(3).

$$y = 76.98x_1 + 78.07x_2 + 70.12x_3 - 134.22x_1x_2 - 169.32x_1x_3 - 5.33x_2x_3 + 65.13x_1x_2x_3 \tag{3}$$

The greater value calculated by regressive equation is, the better overall performance of ink is. As X1=0, X2=1，X3=0, the regressive equation gets the maximal extremum 78.07. It is the same as the formulation2 which can obtain the highest curing rate only by 907. For magenta ink, it can obtain the highest curing rate only by TPO. For black ink, the optimum proportion is TPO：1173=2.12:1. For yellow ink, the optimum proportion is 184:651=1:2.08。

Table1. Formulation experiment and result

NO	X1(651)	X2(907)	X3(1173)	curing rate/%
1	1	0	0	76.98(y1)
2	0	1	0	78.07(y2)
3	0	0	1	70.12(y3)
4	0.5	0.5	0	43.97(y12)
5	0.5	0	0.5	31.22(y13)
6	0	0.5	0.5	60.77(y23)
7	0.33	0.33	0.33	59.53(y123)

3.2 The effect of monomer on the curing rate of UV-curable inkjet ink

UV-curable inkjet inks were respectively prepared by mono-functional monomer EOEOEA, bi-functional monomer TPGDA and tri-functional monomer TMPTA. The curing rate and viscosity of inks were tested. The testing results are shown in figure 2.

Figure 2 shows that the curing rate and viscosity of inks are increasing with the increasing numbers of the groups of monomers. This is because molecular weights of monomers are increasing with the increasing numbers of the groups of monomers, accordingly, intermolecular interactions increase, so the viscosity also increase. Generally, tri-functional monomers have larger activity and higher crosslink density and curing rate. Mono-functional monomers merely can obtain linear polymer after photo-polymerization and have lower curing rate.

The basic demand of UV-curable inkjet ink is low viscosity and high curing rate. In order to get the better overall performance of ink, the ink prepared by the mixed monomer may be considered to make monomers cooperate each other. Because EOEOEA is good to adjust the viscosity of system, TMPTA can make the system has a higher curing rate, and the performance of TPGDA is between EOEOEA and TMPTA, the inks were prepared by EOEOEA、TPGDA and TMPTA with the way of formulation experiment. The result indicates that the optimum proportion is EOEOEA:TPGDA:TMPTA＝5.5:2:1.5.

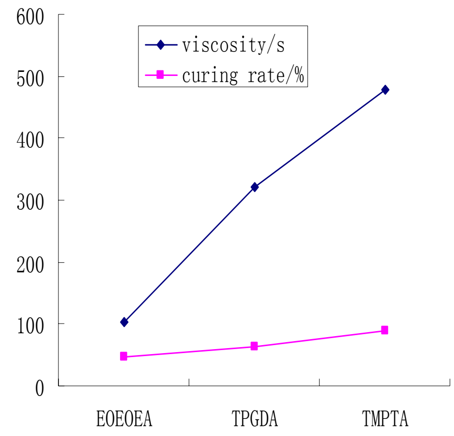

Figure3. The effects of different Monomers on viscosity and curing rate of UV-curable Inkjet Ink

4 Conclusions

The effects of different photo-initiators on the curing rate of UV-curable inkjet ink are different. For cyan ink, the curing rates of inks separately prepared with 651, 907, 1173 are much greater, the optimum proportion is 651:907:1173=0:1:0.For magenta ink, the curing rates of inks separately prepared by photo-initiators TPO、907 and 1173 are much greater, the optimum proportion is TPO:907:1173=1:0:0. For black ink, the curing rates of inks separately prepared by photo-initiators TPO、184 and 1173 are much greater, the optimum proportion is TPO:184:1173=2.12:0:1. For yellow ink, the curing rates of inks prepared by photo-initiators TPO、184 and 651 are much greater, the optimum proportion is TPO:184:651=0:1:2.08.

Through studying on the curing rate and viscosity of inks prepared by different monomers, the mixed monomer which was made up of EOEOEA、TPGDA and TMPTA was designed in this paper, the optimum proportion could be obtained by the way of formulation experiment is EOEOEA:TPGDA:TMPTA＝5.5:2:1.5.

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