Development of New Cationic UV Curable Inkjet Ink

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Two alternative curing mechanisms can be used for UV curable ink: free radical polymerization and cationic polymerization. Although free radical polymerization currently dominates markets, it has an inherent disadvantage: oxygen can inhibit the polymerization. Because of this inhibition, free radical polymerization is limited in application to inkjet systems that employ large ink droplets and high intensity light sources. We have adopted the alternative, cationic polymerization, which is neither inhibited by oxygen nor dependent on light intensity. Combining these advantages with a newly developed cationic-curable monomer, we succeeded in developing a new, unique cationic UV curable inkjet ink for applications that require small droplets even with a low intensity light source. This ink provides flexible images that are suitable for both rigid and flexible media.

1. Introduction

UV curable inkjet systems have proliferated because they can be used with non-absorbing media and because they fix quickly. Two alternative curing mechanisms may be used, free radical polymerization or cationic polymerization. Free radical polymerization currently dominates because of its low cost and the ease of design afforded by a wide selection of usable monomers.

However, free radical polymerization has an inherent disadvantage: oxygen inhibits their polymerization. Inkjet inks have lower viscosity than conventional off-set inks, and atmospheric oxygen can diffuse into inks with lower viscosity. Consequently, inhibition takes place more easily in inkjet inks than in off-set inks.[1)]

To overcome this inhibition, three approaches have been taken. The first is to use a high intensity light source for curing. High intensity light can decompose a great amount of photo-initiators in a short period of time to yield a great enough number of free radicals to overcome the diffused oxygen. Unfortunately, such a high intensity light source is both energy-consuming and costly.

A second approach is to use large ink droplets. The surface area is smaller with larger droplets than with smaller droplets for a given volume of delivered ink. Consequently, the amount of diffused oxygen is smaller with large droplets than with small ones. However, such large droplets can form images with a bumpy surface and can deteriorate image quality.

The third and last approach is to use higher reactive multi-functional monomers. But doing so yields highly cross-linked polymer chains that can lead to inferior flexibility and adhesion.[2)]

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Cationic polymerization, the alternative curing mechanism,[3)] avoids these difficulties by adopting a different polymerization mechanism that is free of oxygen inhibition. We have developed a new cationic UV curable inkjet ink with a newly developed monomer and compared its performance with that of free radical polymerization.[4)] In this paper, we present our results with a focus on curing performance as well as the flexibility of images.

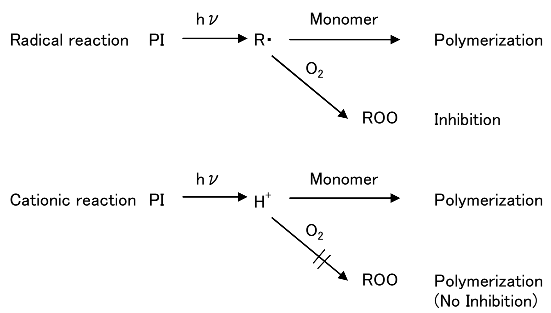

Fig.1 Free radical versus cation polymerization

2. Experimental

Materials

Monomers, di[1-ethyl(3-oxetanyl)]methylether (1), (3',4'-epoxycyclohexan)methyl-3,4-epoxycyclohexan-carboxylate (2), and diethylenediacrylate (3) are commercially available. An epoxy monomer, neopenthyl-glycol di(4-methyl-3,4-epoxycyclohexane-carboxylate) (4), was synthesized by a conventional method.[5)] Photo-initiators, triarylsulfonium salt (5) and triaryl-phosphonium oxide (6), sensitizer, diethoxyanthracene (7), C.I. Pigment Red 122 (8), and polymer dispersant (9) are also commercially available. Most of our evaluations were carried out with the combination of monomer (1) and monomer (4); monomer (2) was used to compare flexibility.

Ink preparation

Pigment (8) and dispersant (9) were dispersed with a beads-mill disperser in a mixture of monomers. The dispersions were then mixed with a photo-initiator and sensitizer. Monomer (1), photo-initiator (5), and sensitizer (7) were used with (2) or (4) to form cationic UV curable inks. Monomer (3) and photo-initiator (6) were used to form free radical UV curable ink.

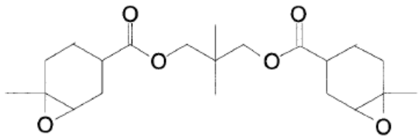

Fig.2 Structure of epoxy-monomer (4)

Evaluation of curing speed

Curing speeds were measured at 25°C under 60%RH or 80%RH with a high pressure mercury lamp (A-bulb) and a low pressure mercury lamp (black light). Coating thickness was varied by changing the size of the wire bars employed. Droplet size was varied with a piezo on-demand inkjet head.

3. Results and Discussions

Effect of coating thickness on curing speed

The effect of coating thickness on curing speed was evaluated for the free radical and cationic inks (Fig. 3). All images were coated with wire bars on PET and cured with a high pressure mercury lamp at 25°C under 80%RH.

The result was that coatings of a given thickness with free radical ink required higher energy to be cured than did those with the cationic ink. In particular, a thin coating of the radical ink required much higher energy.

It has been reported that water molecules can act as chain transfer agents in a cationic polymerization system; water molecules can trap photo-generated acid to terminate polymerization. [6)]

In the results obtained, cationic polymerization took place more effectively than did free radical polymerization, even though the experiments were conducted in high relative humidity. These results suggest that oxygen affects free radical polymerization much more than moisture affects cationic polymerization.

Effect of droplet size on curing speed

The effect of droplet size on curing speed was evaluated (Fig. 4). Both inks were ejected onto PET with a piezo on-demand inkjet head to make single-dot images from 4, 8, 16, and 32 pico-liter (pl) droplets. All images were cured with a high pressure mercury lamp at 25°C under 80%RH.

In much the same manner as with coating thickness, droplets of a given size of the free radical ink required higher energy to be cured than did droplets of the cationic ink. In particular, a small droplet of the radical ink required much higher energy.

The ejected ink was expected to spread out on the media to form thinner images than did hand coatings with wire bars. The thinner ink can be more easily affected by environmental inhibitors, i.e. oxygen for free radical ink and moisture for cationic ink.

Optical microscopic images of the single dots (Fig. 5) reveal that free radical ink produced dot-within-a-dot images, while the cationic ink gave solid dots. In particular, the dot sizes of the dot-within-a-dot images appear larger than those of the cationic ink dots. It may be that oxygen inhibited polymerization at the edges of the free radical dots, with the uncured ink at the edges seeming to be spread out. In fact, the free radical dots spread greatly after rubbing.

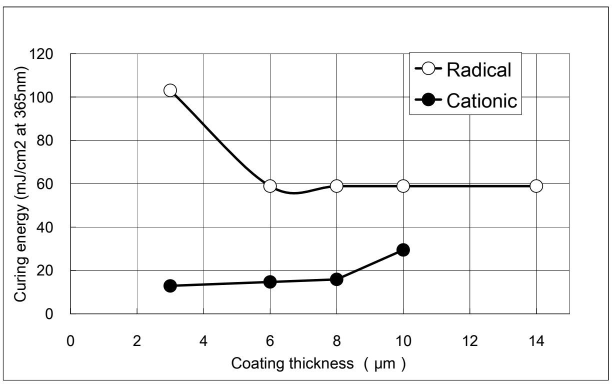

Fig. 3 Effect of coating thickness on curing speed

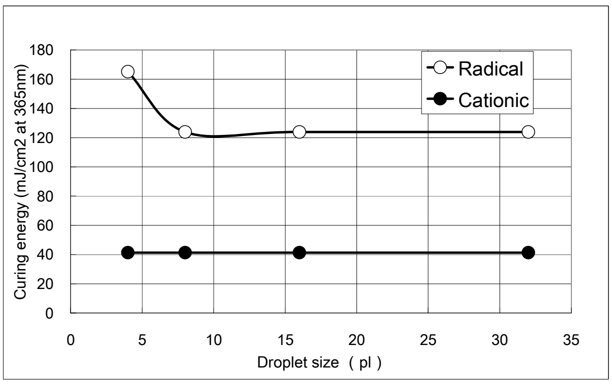

Fig. 4 Effect of droplet size on curing speed

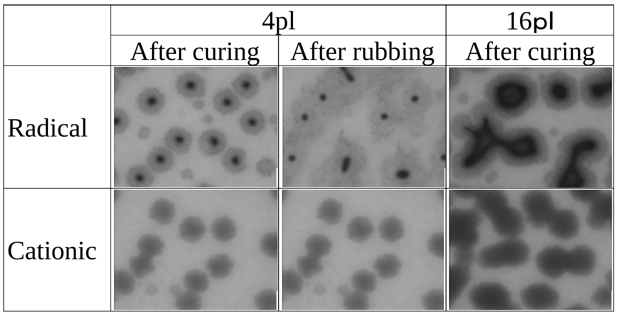

Fig. 5 Optical microscopic images of dots

We also studied the effect of varying the time between ink ejection and curing. For both inks, dot size increased as curing was prolonged. Again, higher energy was required for the free radical ink while relatively low energy was required for the cationic ink.

These results support the aforementioned idea, that oxygen affects free radical polymerization more than moisture affects cationic polymerization.

Effect of light intensity on curing speed

The effect of light intensity on curing speed was evaluated. The free radical ink and the cationic ink were each ejected by a piezo head in 4 pl-droplets on PET and cured with two light sources: a high pressure mercury lamp for high intensity light and a low pressure mercury lamp for low intensity light.

Table 1 indicates that cationic ink was affected only slightly by light intensity, requiring 41 mJ/cm^2 with high intensity light and 50 mJ/cm^2 with low intensity light at 25^{o}C under 60-80%RH. In contrast, the free radical ink was greatly affected. With low intensity light, the ink could not be cured even with prolonged curing.

This sensitivity to light intensity can be understood as an effect of oxygen. Low intensity light yields only a small amount of free radicals which are trapped by oxygen to inhibit polymerization. To overcome this effect, a high intensity light source is widely used with radical polymerization systems.

Table 1 Effect of light intensity on curing energy

	Curing conditions	
Lamp	High pressure mercury lamp (A-bulb)	Low pressure mercury lamp (254 nm peak)
Intensity	500 mW/cm^2	20 mW/cm^2
Radical	165 mJ/cm^2	Not curable
Cationic	41 mJ/cm^2	50 mJ/cm^2

In contrast, the cationic ink can be cured with a low intensity light source, and because no high intensity light source is needed, machine cost is reduced with the cationic polymerization system.

Effect of epoxy monomer on flexibility

The effect of the epoxy monomer on the flexibility of the printed images was evaluated. Two cationic inks were formulated; ink 1 was formulated with the oxetane monomer (1) and with the newly developed epoxy monomer (4). Ink 2 was formulated with the oxetane monomer (1) and the commercially available epoxy monomer (2). The inks were ejected with a piezo head in 4 pl-droplets on polyvinylchloride and evaluated for curing speed, pencil hardness, and adhesion. The inks were also coated by wire bars onto the vinyl to evaluate flexibility.

Table 2 shows the cationic inks performing better than the free radical ink, with lower curing energy for higher curing speed, and with good adhesion.

In particular, ink 1 showed good flexibility while maintaining practical hardness. The fact that the two cationic inks showed similar speeds indicates that both epoxy monomers have a similar reactivity. Therefore flexibility results from the structure of monomer (4).

Table 2 Ink performance

Ink	Ink 1 Cationic with epoxide (4)	Ink 2 Cationic with epoxide (2)
Curing energy	<50 (mJ/cm^2)	<50 (mJ/cm^2)
Hardness	3H	6H
Adhesion	Good	Good
Flexibility	Good	Poor

4. Conclusion

We formulated a radical ink with diethyleneglycol diacrylate and a cationic ink with oxetane and a newly developed epoxy monomer, and evaluated their performances focusing on curing behavior. We also evaluated the effect of epoxy monomers on the physical properties of cured film.

The radical ink showed poor curing behavior because of inhibition by oxygen. In particular, atmospheric oxygen greatly affected thinner coatings and images printed with small ink droplets. The ink at the dot-edge was greatly affected so that resistance to abrasion greatly deteriorated. For the same reason, curing of the ink depended on the intensity of light, with no curing taking place under low intensity light.

Although cationic ink was reported[6] to be affected by moisture, we obtained better curing behavior than with the radical ink even under high relative humidity. Our results suggest that oxygen affects free radical polymerization more than moisture affects cationic polymerization.

Finally, it was found that the newly developed epoxy monomer (4) showed better performance than the commercially available epoxy monomer (2). Ink with monomer (4) polymerizes at a high speed and provides images with practical hardness and good adhesion and flexibility.

Combined, our results indicate that cationic ink containing monomer (4) is suitable for applications that require high image quality. It can be cured even with small droplets of ink to form images with flat surfaces, and it can provide flexible images on flexible media as well as appressed images on rigid materials.

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