Photocurable inkjet ink for printing on metallic and plastic substrates

Mitsuru Ishibashi, Yasuyuki Hotta*, Tohru Ushirogochi*, Ryozo Akiyama**, Kazuhiko Ohtsu**, Hiroshi Kiyomoto**, Chiaki Tanuma**; *Functional Materials Laboratory, Corporate R&D Center, Toshiba Corporation; Kawasaki, Japan; **Core Technology Development Center, Toshiba Tec Corporation; Mishima, Japan*

Abstract

A novel vinyl ether monomer was employed to improve curing properties of photocurable inkjet ink. A cationic polymerization system was used and the improved curing properties using a novel vinyl ether monomer with cyclic ether compounds were demonstrated. The cured UV ink film showed good adhesion on metallic substrates such as stainless steel, copper, aluminum and also plastic substrates. The stability of pigment dispersion in the ink was improved by controlling zeta-potential of the ink. The higher zeta-potential value resulted in stable particle size of the pigment and viscosity of the ink.

Introduction

There is increasing demand for an inkjet printer suitable for on-demand high-speed printing of high-quality images and capable of printing electronic devices. Also, interest in employing rapidly curable ultraviolet-curing inkjet inks (UV inks) has been rising.

For inkjet printing inks, it is necessary for the pigment to be stably dispersed in the ink to ensure discharge stability of the ink from the inkjet head. In order to make reliable pigmented inks offering long-term stability, polymeric dispersants have been widely used [1, 2]. However, it is difficult to maintain long-term dispersion stability in the case of a cationic polymerization UV ink containing a photoacid generator.

On the other hand, the monomers contained in inks have an important bearing on the properties of films printed using the inks. Although the conventional acrylic inkjet inks employing photoinitiated radical polymerization are widely used, they have relatively low sensitivity to UV light and poor adhesion properties.

The rapid photoinitiated cationic polymerization of epoxide monomers has been widely employed in a variety of commercial applications, including UV-curable printing inks [3].

Cationic polymerization of vinyl ethers was examined and also their hybrids with oxiranes were studied [4, 5]. However, UV ink employing the cationic polymerization system has not shown good adhesion property to metal substrate.

In this paper, we report on the efficiency of controlling zeta-potential of pigments to stabilize the pigment dispersion in the cationic UV ink. The improved curing properties using a novel hybrid vinyl ether monomer with cyclic ether compounds are demonstrated and the possibility of using it to manufacture printable electronics is shown.

Experimental

1,2,8,9-diepoxylimonene (C3000), neopentyl glycol digylcidyl ether (SR-NPG), bis(3-ethyl-3-oxetanylmethyl) ether (DOX), and bis-p-diphenyl sulfoniumphenylsulfide hexafluorophosphate (UVACURE1590) were obtained from commercial sources.

2-vinyloxy-6-vinyloxymethyl-7-oxabicyclo［2.2.1］heptane (ONB) was synthesized and obtained from a commercial source. The structure of the novel vinyl ether monomer ONB is shown in Fig. 1.

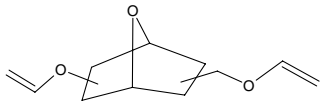


Figure 1. *Structure of ONB*

Pigment was obtained as dispersion in methyl ethyl ketone (MEK) or ONB from a commercial source. All monomers and other chemicals were used as received.

Ink samples were prepared by mixing these monomers, photoinitiator and pigment dispersion to be 4 wt% pigment concentration, and their dispersion stability and photocuring properties were evaluated.

Dispersion Stability

Dispersion stability of cyan ink samples containing SR-NPG (62.5 wt%) and C3000 (37.5 wt%) monomers were examined. Cationic photoinitiator (UVA1590) content was 7.5wt% to the monomers and cyan pigment content was 4wt% to the whole ink. Dispersion stability of ink samples was evaluated by the particle size of pigment (ZetasizerNanoZS, Malvern), viscosity (RE500, Toki Sangyo) and zeta-potential (ELS-8000, Otsuka Electronics) after 9 days keeping at 65 ºC.

Effects of controlling zeta-potential on the particle size and the viscosity stability are shown in Fig. 2 and Fig. 3, respectively. When the value of zeta-potential increased, both particle size and viscosity after 9 days at 65 ºC decreased, which means the stability of pigment dispersion improved. Leaving samples for 9 days at 65 ºC corresponds to storing the samples about 6 months at room temperature.

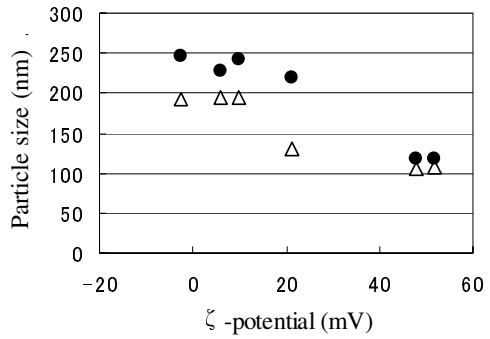


Figure 2. *Effect of ζ-potential on particle size of cyan ink after 9 days at 65 °C. (●) after 9 days at 65 °C, (Δ) after 5 days at room temperature.*

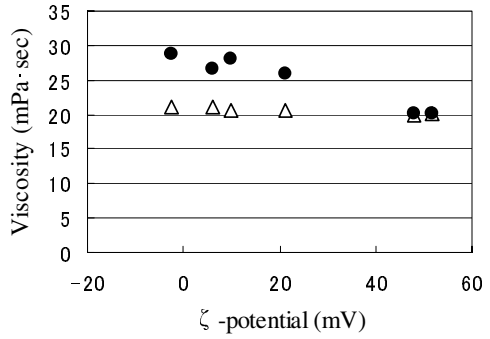


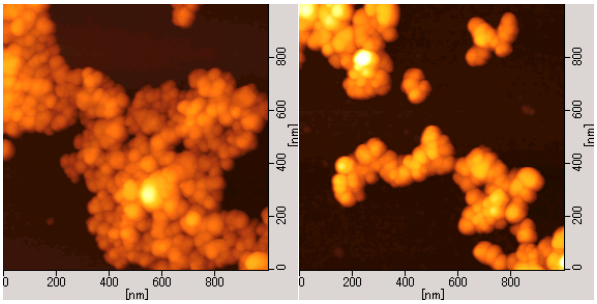
Figure 3. *Effect of ζ-potential on viscosity of cyan ink after 9 days at 65 °C. (●) after 9 days at 65 °C, (Δ) after 5 days at room temperature.*

The zeta-potential value of 50mV resulted in almost the same particle size and viscosity as for the ink left at room temperature. Further increase of the zeta-potential value did not result in any further change.

In Fig. 2 and Fig. 3, the particle sizes and the viscosities after the samples were left for 5 days at room temperature are plotted. These values did not change much within 10 days when the samples were left at room temperature, and therefore, the plotted values are almost equal to the initial values.

High zeta-potential value, namely, above 20mV, resulted in significant change in the particle size of the sample left at room temperature. This means that the control of zeta-potential value is essential for not only maintaining storage stability of pigment dispersion but also for improving particle size of pigment, i.e., to make it fine.

Even if the pigment of another color was used, the stability of the pigment dispersion was improved by controlling the zeta-potential. Fig.4 shows scanning probe microscope (AFM) images of black pigment when the ink samples were left at 65 ºC. The values of zeta-potential were -4.6mV (a) and 13.9mV (b).



(a) (b)

Figure 4. *AFM images of black pigment after 9 days storing at 65 °C when the ζ-potentials of the ink samples were (a) -4.6mV, (b) +13.9mV.*

After storing at 65 ºC, the pigment aggregated tightly when the zeta-potential was -4.6mV. On the other hand, the pigment did not aggregate when the zeta-potential was 13.9mV.

The optimum zeta-potential value for pigment dispersion depends on the pigment. For the black pigment, 13.9 mV seems to be enough to maintain dispersion.

These results show that controlling zeta-potential value of an ink is very important for maintaining pigment dispersion stability and improving particle size, i.e., to make it fine.

Curing Property of ONB Cationic Ink

To improve the printed film properties, the monomers in the UV ink have been optimized. The novel vinyl ether ONB shown in Fig.1 was employed. ONB has two vinyl ether groups and cyclic ether in the main ring.

Table 1 shows some examples of curing properties using ONB with cyclic ether compounds. The ink samples are coated on a metal substrate using a barcoater to realize a film thickness of 6 µm. After photoirradiation by UV lamp (Fusion LH-6, 190 mJ/cm^2), it was heated on a hotplate for further curing. Cured ink films were evaluated by hardness and adhesion properties on various substrates with various heating conditions. The hardness was evaluated by pencil hardness (scratch test, ISO 15184) and the adhesion by cross-cut test (ISO 2409).

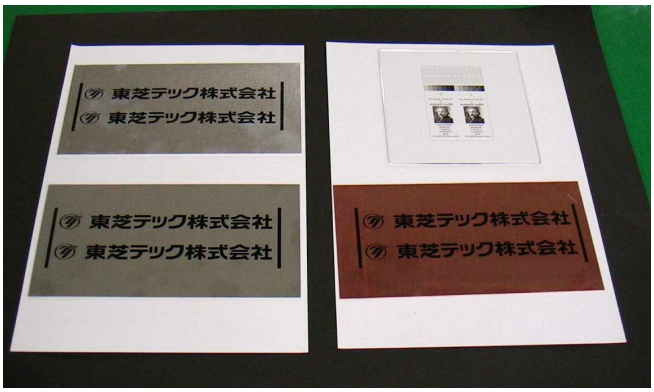
Table 1. Hardness and adhesion of cured ink films.

Substrate	Heat condition	Hardness[a)]	Adhesion[b)]
		UV+Heat	Crosscut
SUS	100℃−1min.	H	1
SUS	100℃−2min.	3H	0
SUS	100℃−5min.	3H	0
SUS	150℃−1min.	F	0
SUS	150℃−5min.	3H	0
Copper	100℃−1min.	3H	0
Copper	150℃−5min.	3H	0
Aluminum	100℃−1min.	H	4
Aluminum	100℃−5min.	3H	0
Aluminum	150℃−5min.	2H	0
OHP film	100℃−1min.	H	0

a) Pencil hardness (scratch test, ISO 15184)
b) Cross-cut test (ISO 2409)

On stainless steel substrates (SUS), 1 minute of heating was not enough to obtain hardness of cured film but adhesion was sufficient. When the heating time was prolonged to 2 minutes, the hardness became 3H in pencil hardness. Sufficient hardness and adhesion was obtained above 100 ºC. On copper substrates, 3H hardness and good adhesion was obtained for only 1 minute heating at 100 ºC. When substrates were aluminum, the classification of adhesion was 4 at 1 minute of heating, which was insufficient. Prolonging heating time to 5 minutes resulted in better hardness and sufficient adhesion.

Thus the ink employing novel vinyl ether ONB showed excellent adhesion property for various metal substrates. On a non-metallic substrate such as a transparency film (OHP film made of surface-treated PET), it also showed sufficient adhesion. The hardness of cured films was improved remarkably by ONB compared with inks containing only epoxides. For example, the cured film hardness of ink containing C3000 and NPG was between HB and F.



(a)

(b)

Figure 5. *Samples printed with ONB cationic ink. (a) Stainless steel, aluminum, glass, copper, (b) PET, PP, PVC.*

The printed samples with cationic ink containing ONB on various substrates are shown in Fig. 5. This ink can be printed on stainless steel, aluminum, glass, and copper plate as shown in Fig. 5 (a) from left column. In Fig. 5 (b), it is shown that the ink is printable on plastic substrates, namely, poly(ethylene terephthalate) (PET), polypropylene (PP), and poly(vinyl chloride) (PVC).

The conversions and hardness of cured film with ONB and other monomers such as C3000 and DOX are shown in Table 2. The conversions are calculated from FT-IR analysis. The IR absorption peaks at 1620 cm^{-1} ($\nu_{C=C}$ of vinyl) for ONB, 851 cm^{-1} (ν_{C-O} of epoxy ring) for C3000 and 982 cm^{-1} (ν_{C-O} of oxetane ring) were used for the calculation.

Table 2. Conversions and hardness of cured film of monomers.

Monomer	Initial photoconversion (%)	Conversion after post-baking (%)	Hardness after post-baking
ONB	94	99	3H
Epoxide (C3000)	50	91	H
Oxetane (DOX)	78	83	F

The initial photoconversion of novel vinyl ether ONB, which is measured immediately after UV irradiation, was very high. The conversion after post-baking was also relatively higher than for other monomers. This indicates that ONB monomer reacted mainly at photocuring. The conversion of C3000 was relatively low and it seems to be mainly reacted at heating.

This result shows that ONB has high sensitivity for photocuring and reacts rapidly. Because of this high reactivity of ONB, the improvement of cured film hardness seems to be accomplished.

The differences between the cationic ink employing ONB and a conventional radical ink are summarized in Table 3. The UV dose necessary to cure the film of 6μm thickness was reduced by employing a cationic curing system and ONB. The adhesion property was drastically improved as mentioned above.

Table 3. Differences between the ONB cationic and a radical UV-curable inks.

	ONB cationic UV ink	Radical UV ink
Sensitivity (UV dose)	190 mJ/cm^2	400 mJ/cm^2
Optical Density	2.0 (Black)	1.3 (Black)
Adhesion	metals, glass, plastics, ceramics	PVC

Applications for Printable Electronics

The developed ink has relatively high optical density at the pigment content of 4 wt%, and therefore, it is suitable for printing color filters in flat panel displays (FPDs) by the inkjet method. The RGB color filter with black matrix was successfully printed in a trial as shown in Fig. 6. The ink can be used for hard coat or insulation films because of its hardness. Since ONB reacts rapidly and hardens by only photocuring, the ink can be used for manufacturing a stacked printed circuit. To stack printed films, it

is necessary to harden the films rapidly for printing the next layer. Combinations with nanometal inks will enable manufacture of printed circuits by the inkjet method.

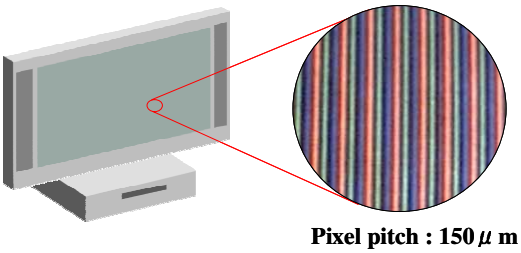


Figure 6. *RGB color filter printed with ONB cationic UV-curable ink.*

Conclusion

It was shown that the control of zeta-potential of ink is important for maintaining storage stability of pigment dispersion and improving particle size of pigment, i.e., to make it fine. The hardness and adhesion properties of cured film were improved by employing novel vinyl ether ONB which has high reactivity. The possibilities of applying ink containing ONB for printable electronics were shown.

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Author Biography

Mitsuru Ishibashi received the B.A. degree in chemistry from International Christian University, Japan, in 1988 and the M.S. degree in chemistry from Tokyo Institute of Technology, Japan, in 1990.

He joined the Corporate R&D Center of Toshiba Corporation in 1990, where he is currently a research scientist in the Functional Materials Laboratory. He has been working on photocurable inkjet ink and its applications in collaboration with Toshiba Tec Corporation since 2003.