High Functionality of UV Inkjet Inks Produced by Combining an N-vinyl Compound

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Abstract

Demand continues to increase for digitized signs such as wide-format indoor and outdoor advertisements, posters, and retail store POPs; such digitized products may be fabricated by vacuum forming or heat forming. To meet the growing demand, the Fuji Film group has conducted research and development projects for highly functional ultraviolet (UV) ink-jet inks. Since 2010, the Fuji Film group has launched a high-sensitivity ink and a vacuum-forming ink. High sensitivity and compatibilty with vacuum forming were accomplished by combining an N-vinyl compound (NVC) with an acrylate compound, which has been widely used in UV ink-jet inks. The purpose of this report is to describe how the NVC contributes to the increased sensitivity and to suitability as a vacuum-forming ink. First, we discuss how the NVC improves the sensitivity of a UV ink-jet ink, then we explain the role the NVC plays in a vacuum-forming ink.

1. Introduction

Since the beginning of the trend toward digital printing around 2000, the use of wide format inkjet printers with UV inkjet ink has expanded in the signage printing market involving wide-format, indoor and outdoor advertisements, posters, retail store POPs, etc. In recent years, the market has been experiencing yet another trend: the subdivision of customer needs such as improved productivity, a wider variety of media types, higher image quality and energy saving.1) Also in the vacuum-formed and heat-formed signage domain that is overdue for digitalization, demand for streamlined processes and graphical design has been increasing and requests are often heard for improvements in the compatibility of UV inkjet ink for vacuum forming. To respond to those requests, the FUJIFILM group has carried out research and development of higher-functionality UV inkjet ink and, from 2010, the group has released products, such as high-sensitivity ink and vacuum-forming ink, for that domain. The high sensitivity of those inks and their suitability for vacuum forming have been realized by introducing N-vinyl compounds (Fig. 1) in combination with the acrylate compounds (Fig. 2) used widely in conventional UV inkjet ink.

The purpose of this paper is to provide an understanding of the functions of N-vinyl compounds in high-sensitivity ink and vacuum-forming ink. First, we verified the mechanism of high sensitivity of UV inkjet ink using N-vinyl compounds. We then studied the functions of N-vinyl compounds in vacuum-forming ink.

2. Functions of N-vinyl compounds in high-sensitivity ink

Including the ink (product code: LL) for the LED-incorporated printer released in 2012, Acuity 1600 LED, our high-sensitivity ink products utilize a characteristic of N-vinyl compounds (NVCs) that mixing them with acrylate compounds at a specified ratio achieves high sensitivity.2) Fig. 3 shows an example of that characteristic. By maintaining NVCs between approximately 20 and 50% of the total polymerizable compounds in ink, the ink film can be made tack-free (no surface sticky) with a small UV radiation count. That is, maintaining the NVC proportion within that range can increase curing sensitivity.

Fig. 1 Example of an N-vinyl compound for UV IJ inks.

Fig. 2 Example of an acrylate compound for UV IJ inks.
Ink using NVCs mixed with acrylate compounds has higher sensitivity than that using one of those two compounds alone. That characteristic mechanism is verified separately for each elementary process of (i) initiation reaction, (ii) propagation reaction and (iii) termination reaction as follows.

(i) Initiation reaction

Table 1 shows the initiation reaction rates of initiator radicals (P radicals generated from acylphosphine oxide) with NVCs and with acrylate compounds measured with the nanotransient absorption measurement method. NVCs had an approximately one-digit larger value for the reaction rate constant than acrylate compounds.

(ii) Propagation reaction

According to the results obtained via real-time IR measurement, NVCs did not promote double bond disappearance by themselves (Fig. 4-1), which indicates that radicals on NVCs are not highly active in polymerization reaction with NVCs. In contrast, mixing acrylate compounds accelerated double bond disappearance (Fig. 4-2). As a result, it can be considered that radicals on NVCs are sufficiently active in polymerization reaction with acrylate compounds.

On the other hand, according to analysis using nuclear magnetic resonance (NMR) spectroscopy of the polymers generated in ink whose NVC and acrylate compound mixing ratio was 30:70, the component ratio of the N-vinyl monomers and acrylate monomers in the generated polymers was approximately 30:70. It is thus indicated that radicals on acrylate compounds can be sufficiently active in polymerization reaction with NVCs.

(iii) Termination reaction

Termination reaction in radical polymerization can be explained by the generation of low-activity peroxy radicals mainly via the reaction between radicals and oxygen. It has not been confirmed yet in the past study whether NVCs have significant differences in reactivity with oxygen, compared with acrylate compounds.

From the analytical results obtained thus far, the mechanism that improves sensitivity of UV inkjet ink with NVCs is inferred as follows. In general, acrylate-base radical UV inkjet ink has low viscosity compared with analog UV ink, such as screen ink, allowing oxygen from the air to easily diffuse into the ink. It is said that the ink is thus strongly affected by oxygen’s inhibiting of polymerization. Therefore, for the improvement of the sensitivity of UV inkjet ink, it is considered to be an effective method to enhance the initiation reaction (i) and the propagation reaction (ii) relatively to the termination reaction (iii) of polymerization inhibition by oxygen. Here, two main observations can be made. Firstly, the high reactivity of NVCs with initiator radicals contributes to the enhancement of the initiation reaction of ink that uses NVCs. However, if ink monomers are composed of only NVCs, the propagation reaction will not progress and the curing sensitivity becomes low because reactivity between NVC radicals and NVCs is low. Secondly, and in contrast, the reactivity of NVC radicals with acrylate compounds is sufficiently high. Mixing the two compounds can thus prevent the slowdown of the propagation reaction. It can be concluded from the above observations that ink using NVCs mixed with acrylate compounds at a specified ratio has higher sensitivity than that using one of those two compounds alone.

Table 1 Initiation reaction rates for the P radical and each monomer; reaction rates estimated by nanotransient absorption measurements.

<table>
<thead>
<tr>
<th>monomer</th>
<th>$k_i \times 10^7 \text{ M}^{-1}\text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NVC</td>
<td>1.7</td>
</tr>
<tr>
<td>TBCHA</td>
<td>0.2</td>
</tr>
<tr>
<td>EOE0EA</td>
<td>0.06</td>
</tr>
</tbody>
</table>

![Graph](image.png)

**Fig. 3** Relation between curing sensitivity and the NVC ratio in total polymerizable compounds in inks.

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3. Functions of N-vinyl compounds in vacuum-forming ink

The vacuum-forming ink (product code: KV) launched onto the market in spring, 2014 has enabled digital-printed decoration to be applied to vacuum-formed products and has brought advantages to many users in the streamlining of manufacturing and development processes and the diversification of design (see Fig. 5 for product examples). The ink’s compatibility with vacuum forming is achieved by a physical property of film: cured film is rigid at room temperature but it becomes flexible enough at high temperatures between 80 and 200°C to be stretched up to 1000%. That characteristic physical property is yet another function given by using NVCs.

Vacuum forming using UV inkjet ink designed for conventional wide format graphics generates cracks in the decoration layer (ink film) (Fig. 6). The cause of the cracking can be explained by insufficient stretchability during forming (at high temperatures) due to the high crosslink density of crosslinked polymers composing the ink film. The verification results obtained thus far indicate that, to give heat stretchability of 1000% or higher (PET substrates/200°C heating), ink with almost no crosslinking components (polyfunctional monomers) is required. That is, the polymerization dilution used in the ink must be composed of only monofunctional monomers.

Vacuum-forming inks provided by other companies consist of only monofunctional monomers. They have achieved an
excellent stretchability at high temperatures by reducing the crosslink density. However, there is a risk of blocking by doing so. Blocking is a problem in which the ink film adheres to substrates when printed matter is stored in piles at room temperature (around 25°C) (Fig. 7). It is necessary for users to exercise proper caution when storing printed matter.

KV ink has succeeded in the prevention of both cracking and blocking by selecting a formulation pattern of two items: no crosslinking components and NVCs. Its cracking and blocking prevention mechanisms are explained below using viscoelasticity measurement results for (1) ink without crosslinking components (including NVCs), (2) ink with crosslinking components and (3) ink without crosslinking components (not including NVCs) and the conceptual images of their polymerized films (Fig. 8).

Ink with crosslinking components (2) has an excessively high elasticity at forming temperatures (greater than 80°C). Therefore, cured ink film cannot adapt quickly enough to the deformation of substrates softened by heating and that causes cracking.

Ink without crosslinking components (not including NVCs) (3) has a sufficiently low elasticity at high temperatures. The film softens to the same extent as substrates by heating. Thus, cracking does not occur during forming. However, elasticity at room temperature is too low, which means that excessively soft film causes blocking when printed matter is stored in piles.

Ink without crosslinking components but including NVCs (1) is equivalent to KV ink. The ink film is composed of linear polymers without crosslinking components. Thus, the film has a low elasticity at forming temperatures (greater than 80°C), allowing sufficient heat softening. In addition, the linear polymers are modified by NVCs. NVCs have a rigid ring-shaped framework and the cured film has a high elasticity as well as a Tg (glass-transition temperature) higher than room temperature. For example, the Tg of NVPs is 80°C and that of NVCs is 90°C. The modification of linear polymers by that rigid framework increases elasticity, achieving a film rigid enough to prevent blocking at room temperature.

4. Conclusion

We verified the functions of N-vinyl compounds (NVCs) utilized in the high-sensitivity ink and vacuum-forming ink we have developed since 2010. The results confirmed that the mechanism to improve sensitivity can be explained by two characteristics: the reactivity between NVCs and initiator radicals is extremely high; and the reactivity of NVC radicals with NVCs is low but that with acrylate compounds is sufficiently high. With regard to NVCs utilized in vacuum-forming ink, it has become clear that they have functions to improve the elasticity of linear polymers at room temperature without increasing the crosslink density.

References


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