Advanced LED UV inks for industrial applications

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Abstract

The technology of inkjet is used not only in house but also in commercial and industrial area. To expand business area, it is one of the main issues that ink is necessary to be used with nonabsorbent substrates such as plastic films. One of solution of this issue is UV ink. The market of UV curable inkjet have shown rapid growth in industrial area, especially in decoration market. We developed UV curable inkjet ink cured by LED lamp, which is able to be used in decoration with inkjet technology. The newly developed ink is superior in stretch to former UV inkjet ink for decoration, and it will be able to be used in forming process with higher curvature. Moreover, the newly developed ink also overcomes the difficulties that the hardness of former UV inkjet ink for stretch forming process is low, and curing coating film is broken off during punching process.

Introduction

During the last decade, inkjet technology has been expanded from home use to commercial printing area such as sign graphic market due to its on-demand feature. Large Format IJ printer with Roll to Roll system which can print on film substrate like PVC is the one of the typical example. Recently, it is also used in industrial printing in production process. Production of color filter for liquid crystal, marking on industrial parts, and painting are a part of examples. The technology supporting this growth of inkjet is UV curable ink. Aqueous ink and solvent ink need drying process to be cured which takes time, but UV ink is able to be cured immediately. Further, it can be used in various substrate. These features is strong point in this market which emphasize productivity.

Difference between UV inkjet ink used in commercial printing and it used in industrial printing is <u>its</u> cured coating film formed by UV curing is required to have function of film when it is used in industrial area. [1] [2] [3] [4] [5]

Selection of UV curing system

There are two UV curing mechanism. One is free radical polymerization, and the other is cationic polymerization. Generally, cationic polymerization is suitable because of its cure shrinkage when sufficient adhesion is required. However, because of low curing speed of cationic polymerization, it is not suitable in industrial market which requires productivity. Moreover, it is effected by humidity, which decreases fast curability seriously. Further, epoxy monomer is too expensive as raw material of UV inkjet ink.

From the above reasons, we chose the other one, radical polymerization. Although radical polymerization is inhibited by oxygen, but it does not have much influence on productivity because the original curing speed is fast enough.

In case that we choose radical polymerization, due to increase of internal stress by cure shrinkage, adhesion to substrate is decreased. However, it is known that it is partially solved by compounding monomer having a cycle ether structure inside of ink. For this reason, radical polymerization is often used for industrial uses. [6] [7] [8]

Table 1 : **Comparison of UV curing mechanisms**

Curing Mechanism	Cationic	Free Radical
Raw Materials	Epoxy, Oxetane Vinyleter	Acrylate Methacrylate
Curing Speed	Late	Fast
Shrinkage	Low	High
Cost	High	Low
Inhibitor factor	Humidity	O2

The picture below shows one example of decoration in plastic molding.

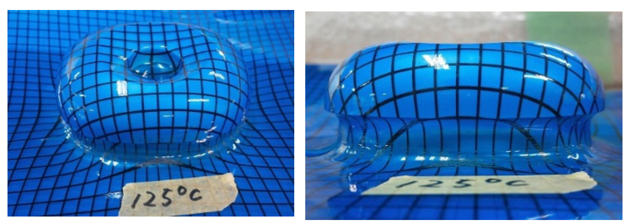

Figure.1 Examples of plastic decoration
Figure.1 Example of decoration molding Ink:Ricoh sample ink. Using heading molding at 120℃

As a temperature of decoration molding, from 100 degree to 200 degree is general, which depends on type and method of substrate. We developed UV ink has high elongation even in high temperature so that it is used with various substrate and method.

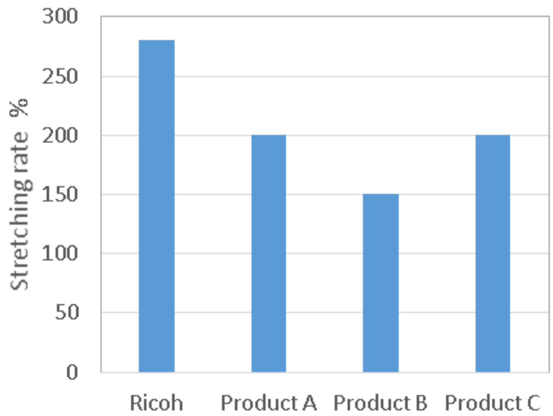

Figure.2 Elongation at 170℃
Base material used：Polycarbonate

Moreover, recently, LED has become common as alternate UV irradiating light source of metal halide lamp. LED lamp is chosen sometimes because of its low electricity consumption and its lifetime. However, the biggest strong point of LED lamp is that substrate is not damaged by heat while curing process with LED lamp which is often happened with metal halide lamp. The figure below shows curability of our newly developed ink with LED lamp.

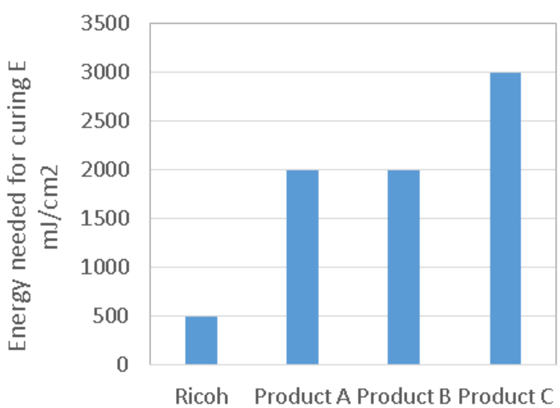

Figure.3 Energy needed for curing LED: 395nm 1w/cm2
Curing property of the worst ink among the CMYKW inks in the ink sets

LED UV Ink Technologies

Elongation

Generally, design of monomer and oligomer is important in composition of UV ink. Design of oligomer is significant considerably, especially in development of UV ink which curing coating film is required to have function. For example, it takes effect in adhesion. As design of oligomer is also important in composition of ink which added elongation to its curing coating film, we verify it in below way.

In composition of ink, in the same compounded amount, we measured degree of effect on molecular weight of difunctional oligomers. (Shown in Figure.4)

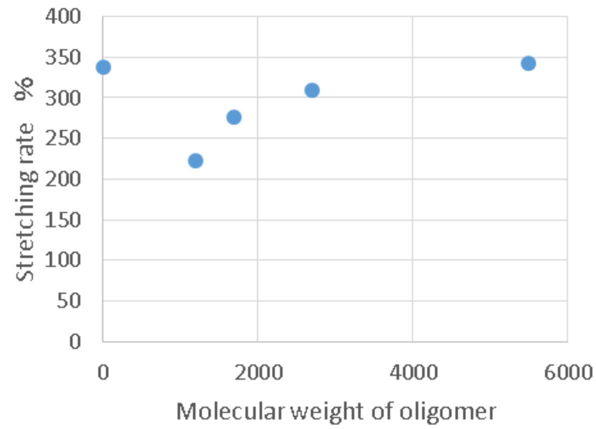

Figure.4 Elongation vs Amount of oligomer
(Ink composition each 5%)

First, when compounded amount of oligomer is zero, ink has high elongation, but also has weak points that durability for scratching is low and curing coating film is broken off during punching process. Secondary, when compound amount of oligomer is the same, higher molecular weight affects more elongation of coating curing film effectively. It is considered that this result is caused by different of number of functional group brought by oligomer. Therefore, high molecular weight oligomer has less number of functional group, which decreased degree of crosslinkage, which makes elongation higher. Thus, evaluation if the same composed amount, effect of oligomer itself may not be measured but there is possibility that effect of functional group is measured.

In order to check the effect of oligomer itself, we performed a verification in which the elongation of the cured film is checked while the number of functional groups is held constant.

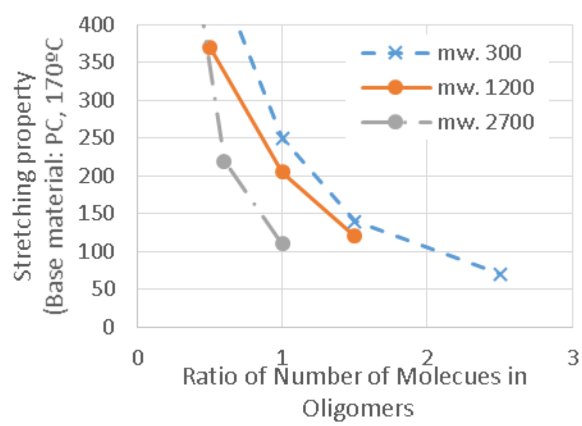

Figure 5 Dependence of stretching property on molecular weight of oligomer Number of functional groups: constant

It can be confirmed from Figure 5 that it is disadvantageous for the elongation to use an oligomer having a higher molecular weight. The reason therefor is considered to be that the elongation is influenced by the solvation in the ink and the conformation of the main chain of the oligomer in curing.

Thus, it can be confirmed from the two results mentioned above that it is advantageous to use an oligomer including a small number of functional groups while having a low molecular weight.

Scratch resistance

As one of features of high elongation ink, sometimes scratch resistance is decreased in lowering degree of crosslinkage to pursue elongation. In order to solve the problem, we performed a verification in which the effect of the molecular weight of difunctional oligomer on the initial hardness of the cured film is checked similarly to the verification of the stretching property mentioned above.

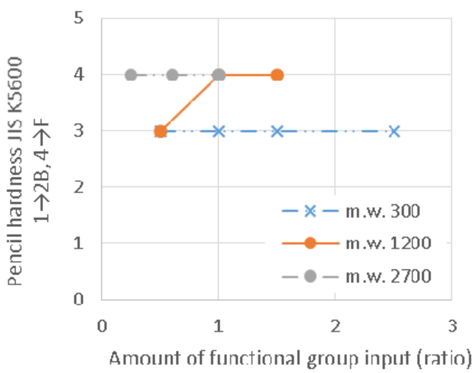

Figure 6 Dependence of pencil hardness on molecular weight when the number of functional groups is the same

As a result of the verification, it was confirmed that when the number of functional groups is the same, it is advantageous to use an oligomer having a higher molecular weight to enhance the hardness. This result is similar to the result in the verification of the stretching property. Namely, we consider that the hardness can be enhanced while being influenced by the degree of solvation in the ink and the conformation of the main chain of the oligomer in curing.

In addition, we attracted attention to the glass transition temperature (Tg) of oligomer to enhance the hardness, and an additional verification was performed.

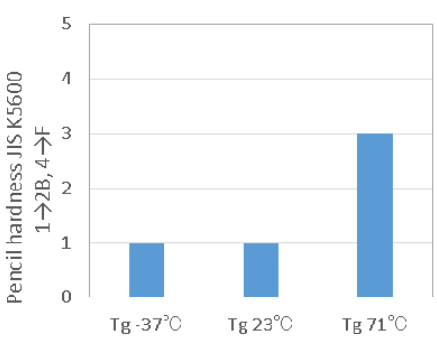

Figure 7 Dependence of pencil hardness on Tg when the number of functional groups is the same

As a result, it was confirmed that by increasing the Tg, the hardness can be enhanced.

Since it was confirmed that the pencil hardness can be enhanced, an oligomer having the two characteristics mentioned above was included in the ink and the cured film was subjected to a scratch resistance test.

Scratch resistance test

The critical load (g) of the cured film was measured using a continuous-loading type scratch tester.

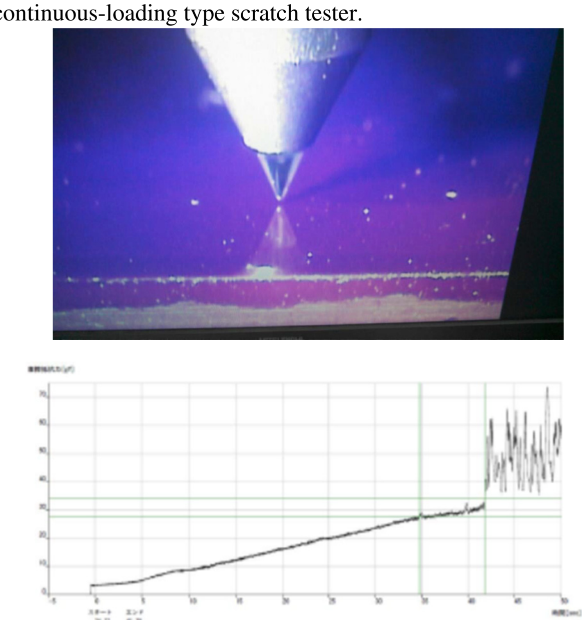

Figure 8 Scratching using a sapphire needle with a diameter of 0.2mm.

The critical load was determined by observing with a CCD camera to determine whether the film is abraded.

In this test, the critical point is defined as the point at which abrasion is started, and the critical load is defined as the load at the critical point.

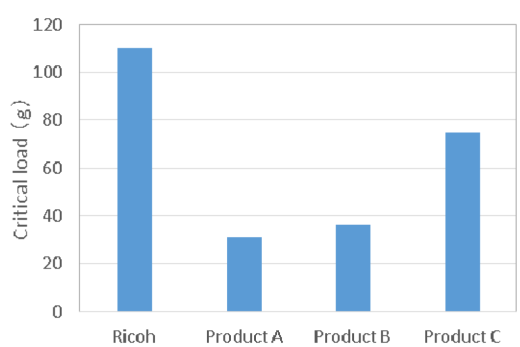

Figure 9 Scratch resistance (critical load)

It was found from the scratch resistance test that by properly designing the molecular weight and Tg of the oligomer added, the scratch resistance of the ink can be enhanced while maintaining the stretching property thereof.

Curability

In order to further enhance the curing ability of a LED UV inkjet ink, it is necessary to add a large amount of initiator to the ink. Since initiators which can be used for LED absorb LED light with a wavelength of from 365 to 395nm, the initiators basically have a yellow color. Therefore, when such an initiator is included in an ink such as white and clear inks in a large amount, the ink or the cured film thereof is tinged with yellow, thereby deteriorating the merchantability thereof.

Additionally, when cured coating film formed by ink compounded large amount of initiator exposed head higher than 70 ℃, unreacted initiator inside of cured coating film get migration, and causes the surface bleed-out, which reduce commercial value often.

Therefore, we are studying to use sensitizer which is able to reduce the amount of initiator, and to prevent ink from being tinged yellow, additionally, it has possibility to get higher curability comparing using the same amount of initiator. The below figure shows curability and the result of b* of cured coating film (d=10 μm).

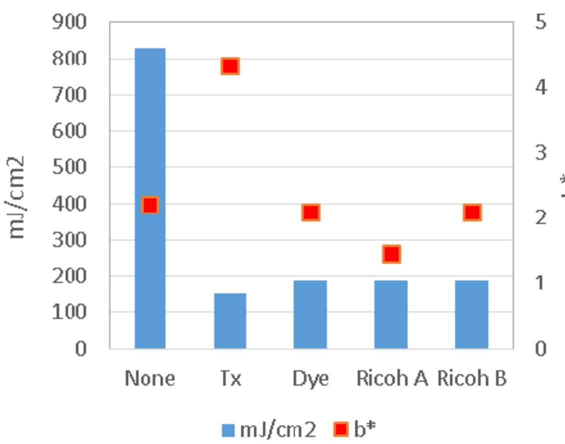

Figure 10: Curability and b* , comparison of type of sensitizer

In this chart, Tx stands for ITX which is thioxanthone compound well known as sensitizer, and Dye stands for Cyannie Dye.
As shown above, we found COMPOUND A and B which able to prevent b* of coated film from increasing, and also decrease curing energy simultaneously (RicohA formulated with COMPOUNDA, RicohB formulated with COMPOUND B). Continuing studying of these compounds, we consider we will be able to provide high productivity ink which has high sensitivity curability in near future.

Conclusion

It has been found that proper amount of oligomer compound in ink is seriously important in order to improve function of UV cured coating film. And, compounding oligomer to ink can prevent cured coating film from breaking off during punching process. Moreover, lower molecular weight oligomer is more effective for improving elongation, and higher molecular weight and higher Tg oligomer is more effective for scratch resistance. And from the view considering market trend to demand higher productivity, we already started to develop sensitizer as well. The newly developed UV-LED ink based on these findings is excellent in curability speed, elongation, and scratch resistance, we expect it provide high value in the decoration molding field.

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Author Biography

Hiroki Nakane received the Master of Science in Chemical from Shizuoka University, Shizuoka Japan in 1998. He was in charge of development of silver-halide photographic products at Research and Development Department in Konica Minolta, Inc. from 1998 and development of ink-jet ink at Research and Development Department in Seiko Epson Corp. from 2007. He has been in charge of development of UV-curable ink-jet ink at Research and Development Department in Ricoh Co., Ltd. since 2013.