A New UV Curable Inkjet Ink : Follow-up Report

Yasuo, Yoshihiro/ Takao, Hiraoka/ Mitsunobu, Morita/ Soh, Noguchi; Ricoh Company Ltd., Ebina, Kanagawa, Japan

Abstract

In various types of inkjet printing ink for an industrial usage, since UV ink is able to produce relatively strong film, it has a potential to be used for printing on a plastic substrates.

In using UV cure ink with radical photopolymerization method, we found a way to improve poor adhesiveness caused by a curing shrinkage by controlling the molecular structure of monomers.

By adjusting the number of molecular weight per methacryloyl group of the monomers, we are able to control the viscoelasticity (tan delta) which represents curing shrinkage and the cured film properties.

As a result, we developed an UV cure ink that could control its cured film property depending on the requirement and could be used in a wide range of applications.

Introduction

Recently, there is a remarkable growth in an inkjet printer market; inexpensive printers that are able to print high grade printed materials are familiarized in an office and a home usage. In addition, inkjet is diversifying its applications for printing on a film or molding products using plastic, metal, glass, and other non-penetrating substrates. For the penetrating substrates like a paper, inexpensive and highly safe aqueous ink is used since it dries while penetrating inside the substrate. On the other hand for non-penetrating substrates, instead of an aqueous ink which needs a large amount of energy for evaporation, a solvent type ink or an UV curable ink is better in terms of a conservation of energy and a compactness of a system. The UV cure ink's characteristic of VOC free has an advantage of reducing the effects on the environment. [1] [2] [3]

There are two major methods of the UV curable ink: free radical photopolymerization (FRPP) method and ion photopolymerization method. For the FRPP method, UV cure ink is widely used in an offset printing and other existing printing systems since inexpensive monomers and photoinitiators for this method are available. Generally, acrylic acid ester is used for a monomer material for a main component of FRPP method UV curable ink. For an inkjet usage, to obtain a good jetting property, the ink has to have a low viscosity. There is a wide variety of commercialized products of acrylic acid ester and there are many raw materials that could be used for the inkjet ink which has a low viscosity. However, it is known that when those low viscous acrylic acid ester touches human skin, it causes allergic symptoms like swell, rash, and itch.[4] Because the acrylic acid ester becomes high molecular weight solid due to the polymerization reaction with an irradiation of UV light in an appropriate condition, there would be no problem consumer touching a final product. On the other hand, since workers handle the UV cure ink in a liquid phase, there is a concern in a physical burden in handling UV cure ink and therefore it is necessary to increase the safety level of the UV cure ink.

In a various ion photopolymerization methods there is a cation photopolymerization method which an epoxy compound or an oxetane compound used as the monomers and a ring-opening polymerization advances a curing reaction. For the ring-opening polymerization, a circular monomer spreads lineally and adds up; therefore volume shrinkage due to a polymeric reaction is relatively small and a residual internal stress in the cured film also becomes small.

On the other hand, since C-C bonds are continuously generated due to an acryloyl group polymerization, the FRPP method has large volume shrinkage as shown in Fig.1 and consequently generates residual internal stress in the cured film and decreases the adhesiveness.

As stated before, in addition to the safety issue, the improvement in adhesiveness to the various kinds of substrates is required.

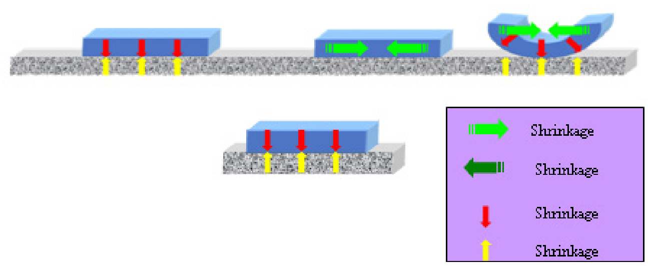


Figure 1. Schematic model of the interface between UV cured ink and a substrate

Safety issue of a monomer

For the UV ink for inkjet using RPP method, we found a trend, by testing few hundred kinds of metharylic acid ester monomer material, that if a monomer used as a main component of the ink has a small molecular weight, then the skin sensitization becomes worse as shown in Fig. 2.

Since a molecular weight of a monomer and a viscosity are closely related, the trend we found concludes that it is difficult to achieve both properties at the same time: the raw material for inkjet ink has to have low viscosity and the degree of skin sensitization has to be low.

However, we obtain relatively good results to solve this problem by using of methacrylate ester (ester of methacrylic acid).

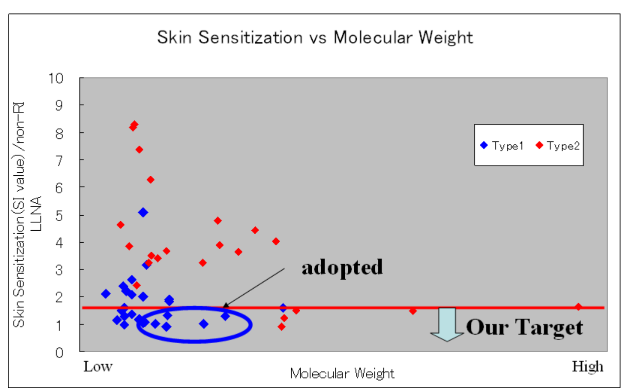


Figure.2. Effect of molecular weight for skin sensitization of (meth)acrylates

As shown in Fig.3, we conducted a skin irritation test which is known as causing a symptom of chemical burn injury and obtained the results as similar to the skin sensitization test results: smaller the molecular weight, worse the skin irritation.

However, not as difficult as skin sensitization, we confirmed that there are various kinds of methacrylic acid ester available which could solve both the safety issue and the viscosity (low molecular weight) issue.

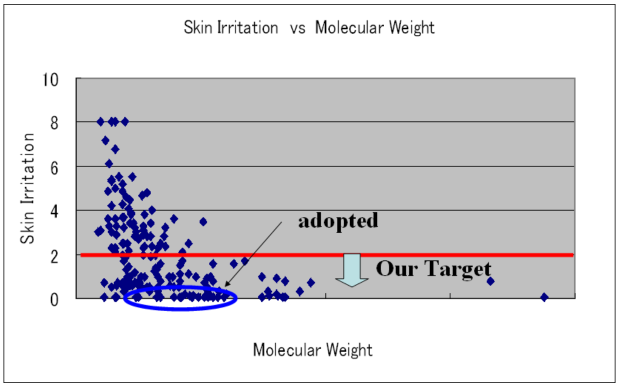


Figure.3. Effect of molecular weight to the skin irritation level of (meth)acrylates

When you use low viscous acrylic acid ester as a main component, it is difficult to achieve sufficient safety level for both skin sensitization and the skin irritation; therefore, we designed an ink that exclude causative substance of the skin sensitization by using methacrylic acid ester. Methacrylic acid ester is a material used for a dental therapy and therefore we expect safeness of using this material for the printing system. Even though the methacrylic acid ester generally has a poor photopolymerization property, we succeeded developing the UV cure ink for inkjet with a good jetting ability by selecting relatively better photopolymerization property material and by optimizing the composition formulation of accessory components. In addition, besides the skin sensitization and the skin irritation, we succeeded developing the UV cure ink that uses materials that has sufficiently small acute oral toxicity (a test for an accidental ingestion) level, and negativity in mutagenicity (represents the biological cell mutation and a risk of carcinogenicity); we expect to decrease a physical burden of workers who work long hours in a printing manufacturing scene using UV cure ink.

Residual internal stress in a cured film

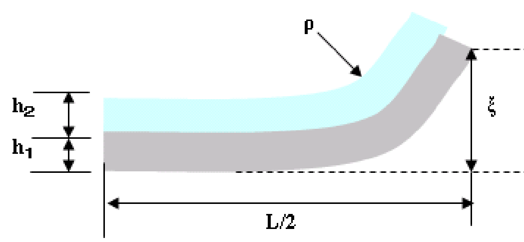
Selecting a monomer material by emphasizing the safety level, we developed a clear UV cure ink for a top coater that would add glossiness and increase a design value of a graphics on a plastic substrate. Under the assumption of this product will be fabricated, we machine cut the work. As shown in Fig.4, graphic layer under the top coated layer peeled at the cut off edge and ended up losing the design value.

Figure.4. Photographic image of a cut off edge of a UV clear top coating film

To investigation the cause of the peeling, we used same sample and hand cut the top layer and confirmed that the graphic layer peel off and flew apart. On the other hand, we hand cut the sample without the top coating but there is no peeling and no obvious damage at the cut off edge. We proposed a hypothesis, that a residual internal stress, which is strong enough to fly the peeled part of the layer, in the top coat layer is causing the peeling at the cut off edge. We attempted to solve the peeling problem by controlling the residual internal stress of the cured film by adjusting the composition and selecting the appropriate kinds of methacrylic acid ester.

Evaluation of curing shrinkage force

To simplify the experimental procedure, we calculated the residual internal stress due to the curing shrinkage by measuring the curl height of the top coat layer on a thin film substrate. We calculated the internal stress due to curing shrinkage by using the equations shown in Fig.5 [5]



$$\rho = L^2/8\xi + \xi/2 \fallingdotseq L^2/8\xi$$

$$\sigma_c = E_1 h_1^3/12h_2 \times 2/\rho(h_1+h_2) \times [1 + 1/3(h_1/(h_1+h_2))^2]$$

$$\sigma_c = E_1 h_1^3/12h_2 \times 16\xi/L^2(h_1+h_2) \times [1 + 1/3(h_1/(h_1+h_2))^2]$$

Figure.5. Calculation model and equations of the internal stress due to curing shrinkage

From the equaitons shown in Fig. 5, we know that the internal stress and the curl height are proportionally related.

We found the relationship between the residual internal stress and the acrylic equivalent amount, which is a unique material property for a monomer that is closely related to a cross-linked site molecular weight and is generally known as [molecular weight / number of functional group.

From this result, we formulated an ink which has the large acryloyl equivalent amount to reduce the residual internal stress.

Since we now know that the internal stress and the curl height are proportionally related, we simply compared the level of curl heights to validate the level of internal stress.

Ink formulation

In designing ink formulation, we generally mix various kinds of monomers in order to fulfill various requirements; we calculated those mixed monomer's acryloyl equivalent amount as an average mole of composition ratio of different kinds of monomers. We evaluated the acryloyl equivalent amount effect the viscoelastic property of the cured film which we think this property is related to the mechanism of producing internal stress.

As shown in Fig.6, we obtained a clear top coat that has a sufficient fabrication property (no more peeling and chipping at the cut down edge) by using the second largest average acryloyl equivalent amount formulated ink .

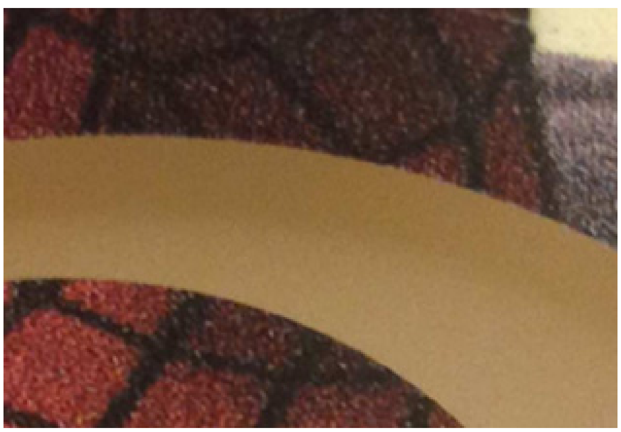


Figure.6. Photographic image of cut down edge of the clear top coating

We successfully showed the example of solving a fabrication property problem of the cured film by testing the hypothesis and by controlling the internal stress.

Conclusion

We confirmed that we are able to control the residual internal stress of the cured film by formulating the RPP UV ink with adjusted average acryloyl equivalent amount of monomers.

We would like to expand our research in formulating UV cure ink for various kinds of substrates that is difficult to obtain strong adhesion (i.e. polyethylene, polypropylene, etc.), substrates with flectional application, and other various required specifications and applications.

References

[1] N.Caiger and S.Herlihy: Oxgen Inhibition Effects in UV-Curing Inkjet Inks, IS&T's NIP 15: International Conference on Digital Printing Technologies, 116-119 (1990).

[2] A.Tomotake, T.Takabayashi, N.Sasa, A.Nakajima, and S.Kida, Proceedings of NIP24: International Conference on Digital Printing Technologies and Digital Fabrication 2008, 532-534 (2008).

[3] M.Ishibahi, Y.Hotta, T.Ushiroguchi, R.Akiyama, K.Ohtsu, H.Kiyomoto and C.Tanuma: Photocurable inkjet ink for printing on metallic and plastic substrates. IS&T's NIP 23, 134-137 (2007).

[4] R.J. Dearman, C.J. Betts, C. Farr, J. McLaughlin, N. Berdasco, K. Wiench, and I. Kimber: Comparative Analysis of Skin Sensitization Potency of Acrylates (Methyl Acrylate, Ethyl Acrylate, Butyl Acrylate, and Ethylhexyl Acrylate) Using the Local Lymph Node Assay, CONTACT DERMATITIS, 57, 242-247 (2007)

[5] Mitsukazu OCHI; Kazuaki ONISHI; Kiichi YAMASHITA; Masaki SHIMBO (Faculty of Engineering, Kansai University),Title: Internal stresses in UV-cured epoxide resin coatings.Source: KOBUNSHI RONBUNSHU; ISSN:0386-2186; VOL.47; NO.7; PAGE.559-567; (1990)

Author Biography

Yasuo Yoshihiro joined Ricoh Company LTD,. in 2010., He has been developing UV curable inkjet inks now.

Takao Hiraoka joined Ricoh Company LTD., in 2008. He has been developing UV curable inkjet inks now.

Mitsunobu Morita joined Ricoh Company LTD,. in 1990. He has been developing functional materials.

Soh Noguchi joined Ricoh Company LTD,. in 1998. He has been developing functional materials.