

How the Selection of Raw Materials Can Impact Print Speeds in Digital Printing

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Abstract

Faster cure speed and rapid property developments are a few of the drivers that will need to be improved for UV inkjet to unlock new printing applications in packaging and variable data printing. This paper will highlight how the raw material selection in UV inkjet inks directly impacts structure property and speed.

1. Introduction

The digital printing process involves jetting tiny droplets of ink from the orifices of printhead nozzles onto a substrate which are varied depending on the application¹. Radiation curable ink droplets are cured using ultra violet (UV) light to form a permanent print. For the digital printing process ink viscosities are very low (typically < 30 cps at room temperature.) The printheads that allow the ink to be deposited are viscosity specific. At a jettable temperature of 40 - 45°C the ink viscosity needs to be between 8 – 14 cps. Furthermore, depending on the application, the ink will need to exhibit specific properties such as color gamut, chemical & abrasion resistance, flexibility and adhesion. One of the typical problems associated with inks is poor adhesion over non-porous or low surface energy substrates including vinyl and polyolefin films. As an example, polypropylene banner material is widely used for trade-show and event graphics, banner stands and point-of-purchase (POP) advertising. Due to the low surface energy of polypropylene, materials such as acrylic monomers do not wet these substrates well and as a result display poor adhesion. The inks need to display good interfacial adhesion, especially if printed on to a white ink layer. Thus, formulating low viscosity digital inks enabling both material and jetting properties is a challenge. Furthermore, properties such as rheology, pigment particle size, surface tension of the ink and its long term stability are all important factors that need to be carefully tailored in designing the ink. These inks also have to match the printhead performance characteristics so that it exhibits a wide jet operating window. In many instances the ink needs to display faster print speeds so as to be useful in applications requiring single pass printing for variable data as well as in printing over labels.

The present study on digital ink formulation is mainly centered on graphic arts application for signage and Point of Sale (PoS) as well as for printing over banner substrates for billboard applications. Initially, jettable over print varnishes (OPV, also referred as clear ink) were formulated with wide ranging oligomeric and monomeric acrylated materials, so as to ascertain the properties these materials would display in an ink composition for printing over both rigid and flexible substrates for the graphic arts applications.

Print speed is a critical performance parameter in ink jet for both wide and grand format printing. The gap between the printhead and the printed article is < 2 mm due to the requirements of drop straightness and placement. Despite the relatively short dwell time before curing, oxygen can inhibit surface cure. It is well known that oxygen causes incomplete cure at the surface causing poor surface properties rendering the printed articles useless². Amino acrylates are known in this respect to flood the surface with active radicals scavenging the oxygen from the air which form peroxy radicals and prohibits chain growth. These amino acrylates also have active hydrogen that form new radicals initiating a new chain, thus rendering complete surface cure, as shown in Figure 1. In this regard we have investigated several amino acrylates with wide ranging viscosity and functionalities, shown in Table 1. Furthermore, the higher viscosity nature of these materials have to be taken into account in the inkjet formula to keep the ink viscosity below 30 cps.

| Amino Acrylates | Functionality | Viscosity mPa. s @ 23°C |
|-----------------|---------------|-------------------------|
| AA-1 | 2.9 | 50 – 90 mPa .s |
| AA-2 | 2.9 | 1000 - 3000 |
| AA-3 | 3.5 | 300 - 600 |
| AA-4 | 2 | 2500 -4000 |
| AA-5 | 3.4 | 2500 - 3500 |

Table 1. Amino acrylates in inkjet formulas

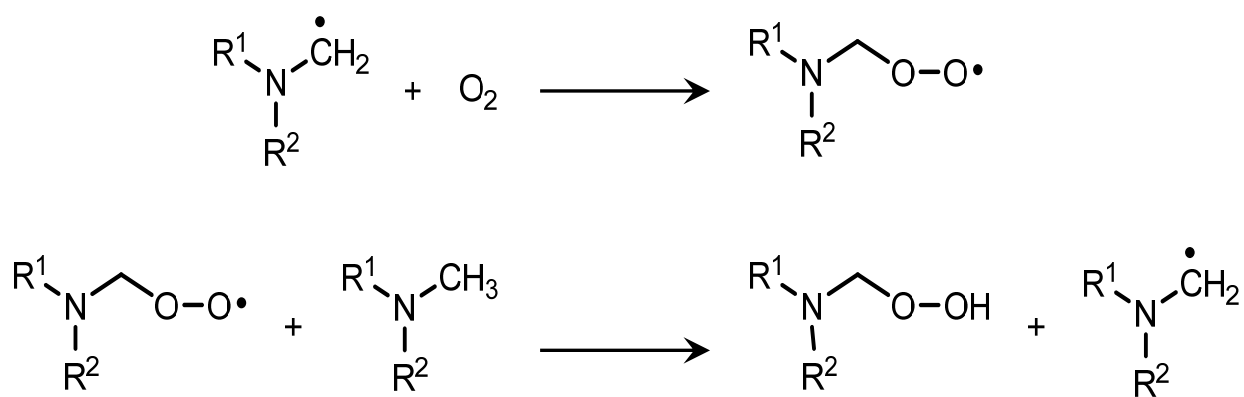


Figure 1. Mechanism of amino acrylates to control oxygen at the surface

1.1 Materials

For this study in designing an ink jettable formulas all acrylates and photoinitiators³ (PI) were obtained from BASF Corporation. The main purpose of this project was to study the effect of amine modified polyether acrylates (also referred as aminated acrylates) in jettable formulations. The goal was to enhance cure speed while maintaining low viscosity needed for ink jet applications. The information would be very useful for ink formulators to design pigmented inks for specific applications requiring speed and performance.

Also, ITX (Isopropylthioxanthone) is commonly used in printing inks “as is” or as a sensitizer for α -hydroxy ketones (AKH) to enhance cure speed and provide the desired material properties to an ink or a coating⁴. However, as ITX is not incorporated into the network structure it is known to migrate over time. This could be detrimental especially in application that require food safety⁵. Since most of the applications in digital are tailored towards graphic arts market for signage application⁶, it may be a less of an issue but certainly worth further investigation to find alternatives. As a result, we wanted to investigate if Irgacure® 500 along with other α -hydroxy ketone (AHK) could be an option in application involving inkjet printing.

Initially, jettable OPV’s were formulated with a wide range of oligomers, mono and difunctional monomer types to understand ink performance properties, (i.e. in the absence of pigment). The types of materials used in the present study and their functions are provided in Table 2. Properties such as adhesion and chemical resistance over a wide range of plastic substrates were thus investigated along with cure speed and viscosity. The experiments described herein provide information on an optimized photoinitiator package for digital inks for graphic arts application. The information obtained would be useful in formulating process colored inks using some low migrating photoinitiators and will also be the focus of the presentation.

| Chemistry | Function |
|---|---|
| Urethane acrylate, Laromer® LR 8987 | Hardness, chemical resistance and weathering |
| Amino acrylates (AA-1 – AA-5) | Cure speed |
| Tripropylene glycol diacrylate (TPGDA) | Diluent, F=2 |
| Hexane diol diacrylate (HDDA) | Diluent, F=2 |
| N-vinyl Caprolactam (NVC) | Diluent, F=1 |
| Phenoxy ethyl acrylate (POEA) | Diluent, F=1 |
| Polyether modified Acrylate (Ethoxylated TMPTA) | Reactivity, F = 3 |
| Quinone Methide (Irgastab® UV 22) | In-can Stabilizer |
| BAPO (Irgacure® 819) | Through cure photoinitiator |
| Dual functional Oligomeric AHK (Irgacure® LEX-201) | Low migration, α -Hydroxy ketone (AHK) photo initiator |
| Di-functional AHK (Irgacure® 127) | Low migration α -Hydroxy ketone photoinitiator |
| AHK + Benzophenone (Irgacure® 500) | Type I, II photoinitiator |
| Modified Polysiloxane (Efka® SL3257) | Wetting agent |

Table 2. List of ingredients in clear ink jettable composition

2. Experimental

Inks were made by adding oligomers, photoinitiators and additives to low viscosity monomers. The mixtures were heated in a 60°C oven and mixed well using a speed mixer at 2500 rpm for 2 minutes.

Wet drawdowns were made using a #2 K rod (~ 12 μ ink thickness) over plastic substrates, and cured using Heraeus HP-6/LC-6, (DRS-10/12, P/N SC61469DRS) Fusion 300 Watts/in D Lamp at varied % power at a belt speed of 77 feet / min. Cure speed was determined by rubbing a cotton Q-tip aggressively over the cured surface on a polycarbonate substrate until no smudge was observed. Cross hatch adhesion test was done on the cured ink after conditioning for 16 hours at room temperature. Ink viscosities were determined via CAP-2000+ Brookfield Cone and Plate viscometer using spindle #1 at 500 sec⁻¹ and are recorded in mPa.s.

3. Results

In digital inks, typically due to the viscosity constraints, the use of high levels of oligomers is restricted. The material properties are achieved via a combination of minimal amount of oligomer with higher amounts of low viscosity monomers. The cure speed is dictated by a combination of aminated acrylates with a right blend of photoinitiator to display good surface and through cure properties⁷. TPGDA was used in the formula, due to its being useful as a vehicle for dispersion during the pigment milling process and also due to its ability to wet the pigment in aiding efficient milling. The starting ink formula is depicted in Table 3.

| Materials | Amount |
|-------------------|--------|
| Urethane Oligomer | 4 |
| HDDA | 52.9 |
| POEA | 5 |
| Ethoxylated TMPTA | 4 |
| AA-1 to AA-5 | 5 |
| TPGDA | 15 |
| Irgacure 819 | 2 |
| Irgacure LEX-201 | 8 |
| Irgacure 127 | 1 |
| ITX | 2 |
| Efka SL 3257 | 0.1 |
| Irgastab® UV 22 | 1 |
| Total | 100 |

Table 3. Formulation for a jettable clear ink jettable composition

3.1 Effect of amine polyether acrylates on cure speed

Since many of the applications in inkjet will require inks to cure at speeds of 250 ft. / min or faster, the ability to cure a 9 – 12 micron ink at optimum speed is critical. Several aminated polyether

acrylates, were investigated. These aminated polyether acrylates are known to enhance cure speed especially in conjunction with both Type I and II photoinitiators, via overcoming the effect of oxygen inhibition at the surface of the film. Aminated polyether acrylated materials used during the study are listed in Table 1. Based on this study we find that AA-4 by far exhibits the fastest cure speed. Figure 2 depicts viscosity and cure speed represented as 1/Exposure (cm^2 / mJ) with respect to various polyether acrylates at 5% in the clear ink. The higher viscosity lower functional AA-4 compared to higher functional lower viscosity AA-3, gave inks of similar viscosities. However, the cure speed of the ink containing AA-4 is ~ 4 times faster than ink containing AA-3 which exhibits cure speed similar to other aminated acrylates evaluated from Table 1. The use of these amine acrylates did not show any detrimental effect on adhesion and chemical resistance upon curing, over wide variety of plastic substrates such as Polyvinyl chloride (PVC), Polycarbonate (PC), Polystyrene (PS), CoroplastTM (CO) and Polypropylene (PP), as shown in Figures 3 and 4, but exhibited poor adhesion over Polyester (PE) and was the subject of further investigation. As a result we undertook the study to investigate various mono functional monomers including N-vinyl caprolactam (NVC) in the presence of aminated polyethers acrylate AA-4 at 5% level in the ink formulation.

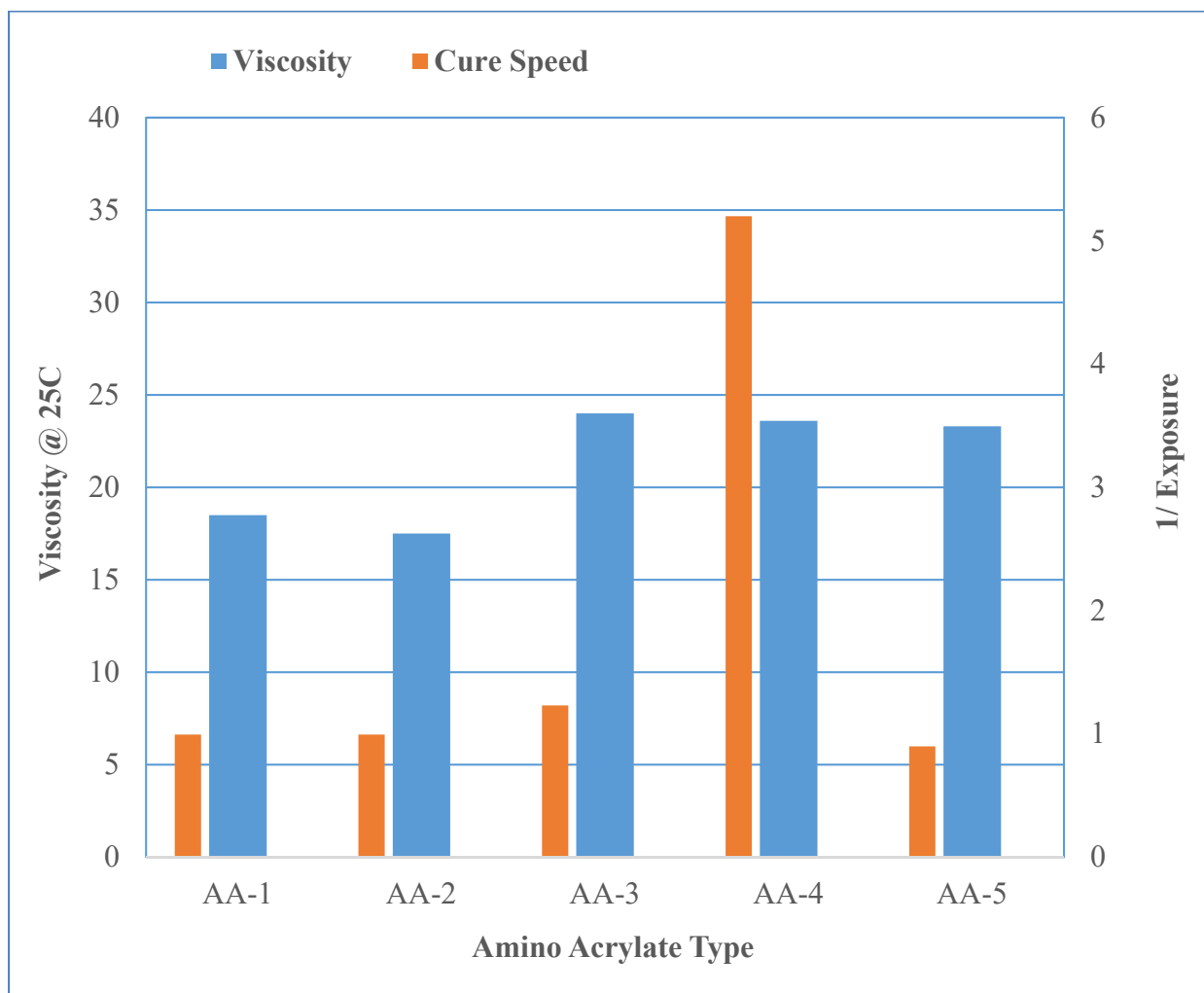


Figure 2. Viscosity vs. cure speed for clear inks containing amino acrylates

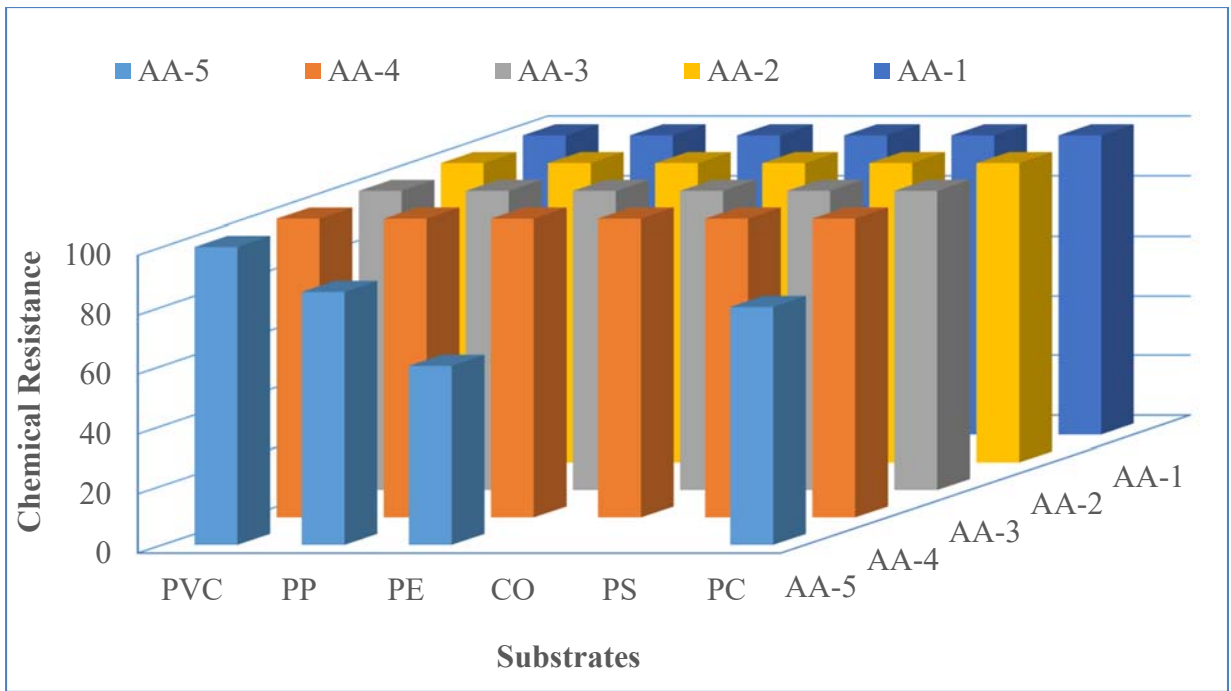


Figure 3. Chemical resistance of cured clear inks containing amino acrylates

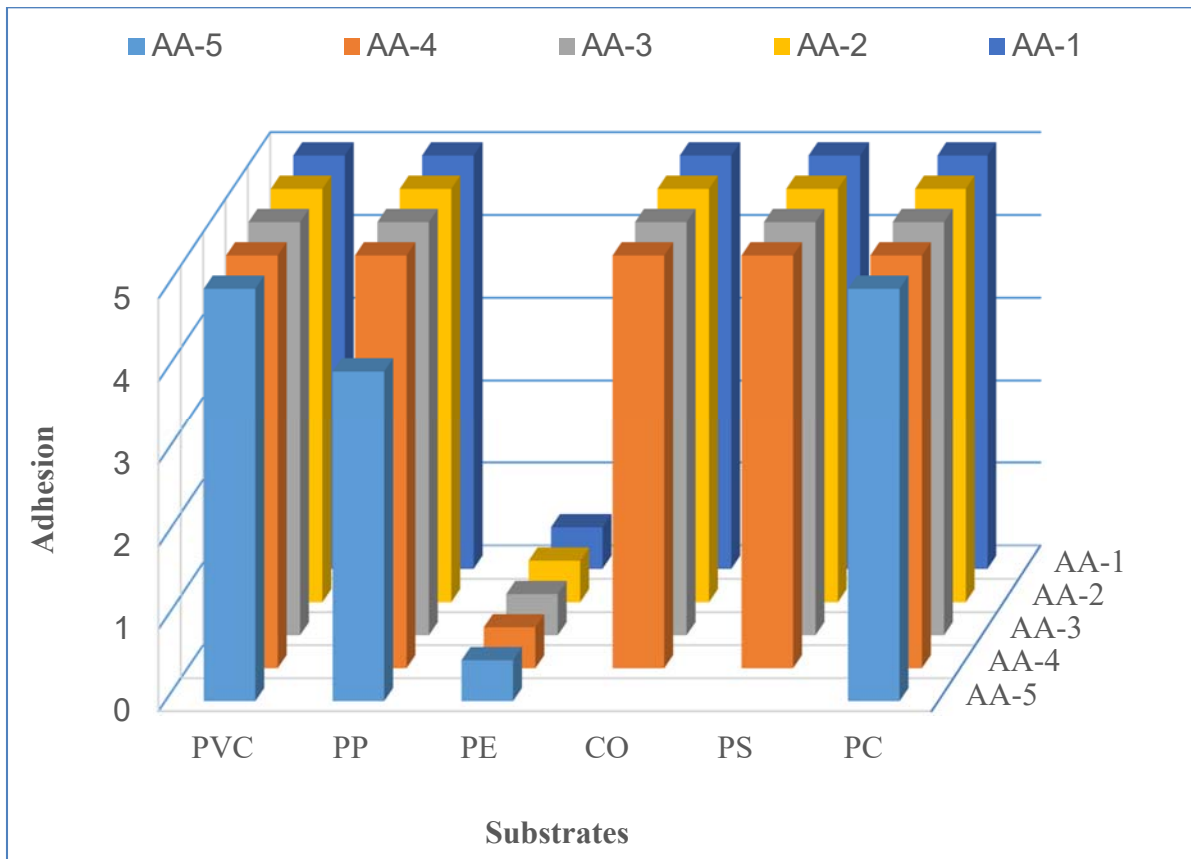


Figure 4. Adhesion of cured clear inks containing amino acrylates

3.2 Effect of monomers in jettable clear inks

Although the amount of mono-functional monomer is present at low levels in these formulas, it does exhibit influence on viscosity, cure (Figure 5) and more so on adhesion over polyester substrate, as shown in Figure 6. Several mono functional monomers were investigated in clear ink compositions such as; Laromer® POEA, TBCH, LR 8887 and NVC as well as traditionally slower curing vinyl ethers including DVE-2, DVE-3, at 5% level. Both DVE-2 and DVE-3 enabled lower viscosity inks similar to an ink with NVC. Although adhesion over certain plastic substrate is an issue (Figure 6), no significant effect is observed on the crosslink density. Furthermore, the presence of vinyl ethers and NVC do influence viscosity to some extent but definitely influence cure speed, plotted as 1/Exposure (cm^2 / mJ). So the formulations derived from vinyl ethers and NVC cure somewhat faster than POEA, TBCH as well as LR 8887, as is shown in Figure 5. The inks overall displayed great chemical resistance, but inadequate adhesion over polyester. This is more so for inks derived from DVE-2, DVE-3 and NVC. However, increasing the NVC content from 5 % to 45% helped in developing adhesion across many different plastic substrates including Polyester, Coroplast™ and Polypropylene without affecting chemical resistance or cure speed (Figure 7). The ink viscosity was between 20 -21 cps at 25°C, showed minimum influence with increasing NVC content.

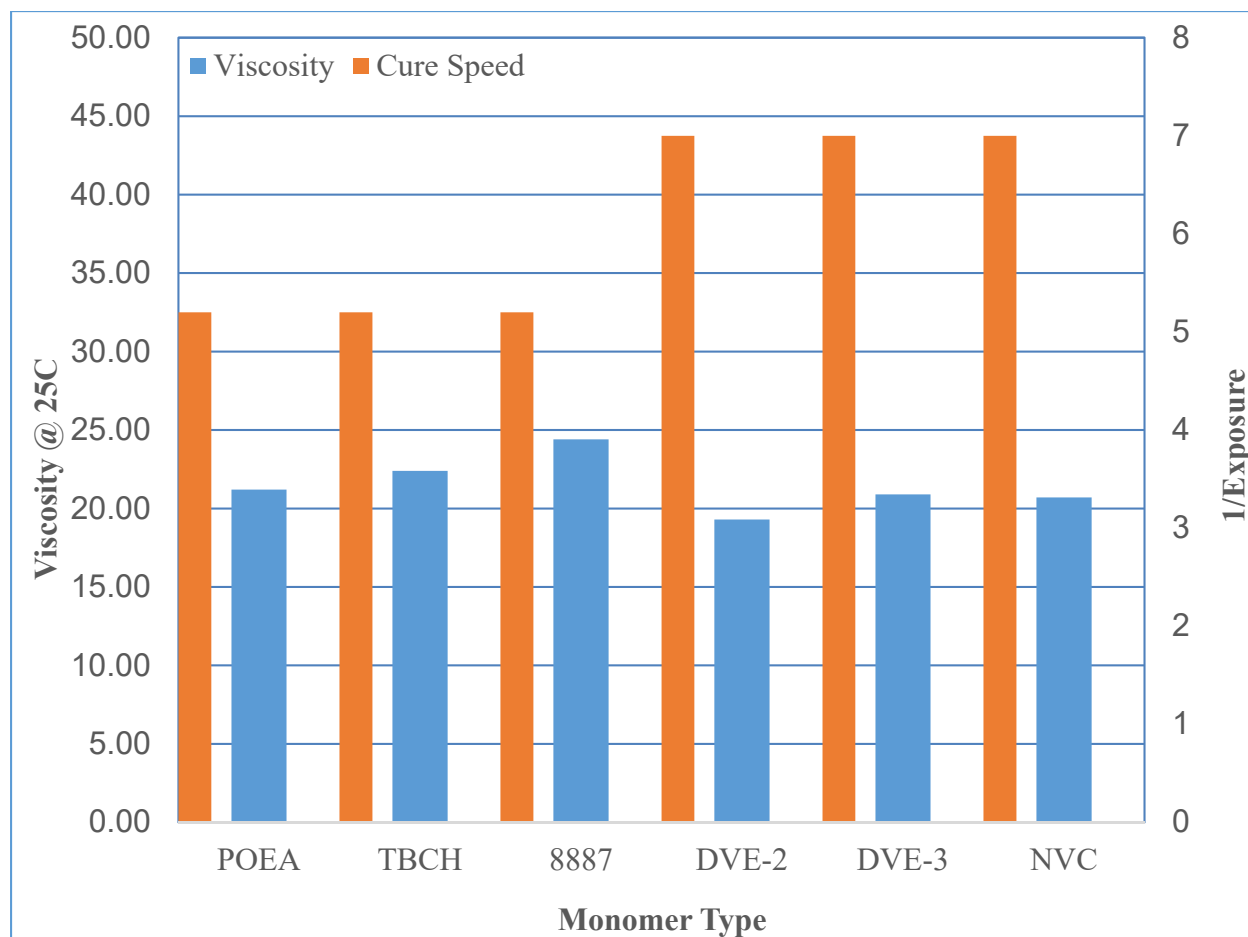


Figure 5. Viscosity vs. cure speed for ink containing mono acrylates and vinyl ethers

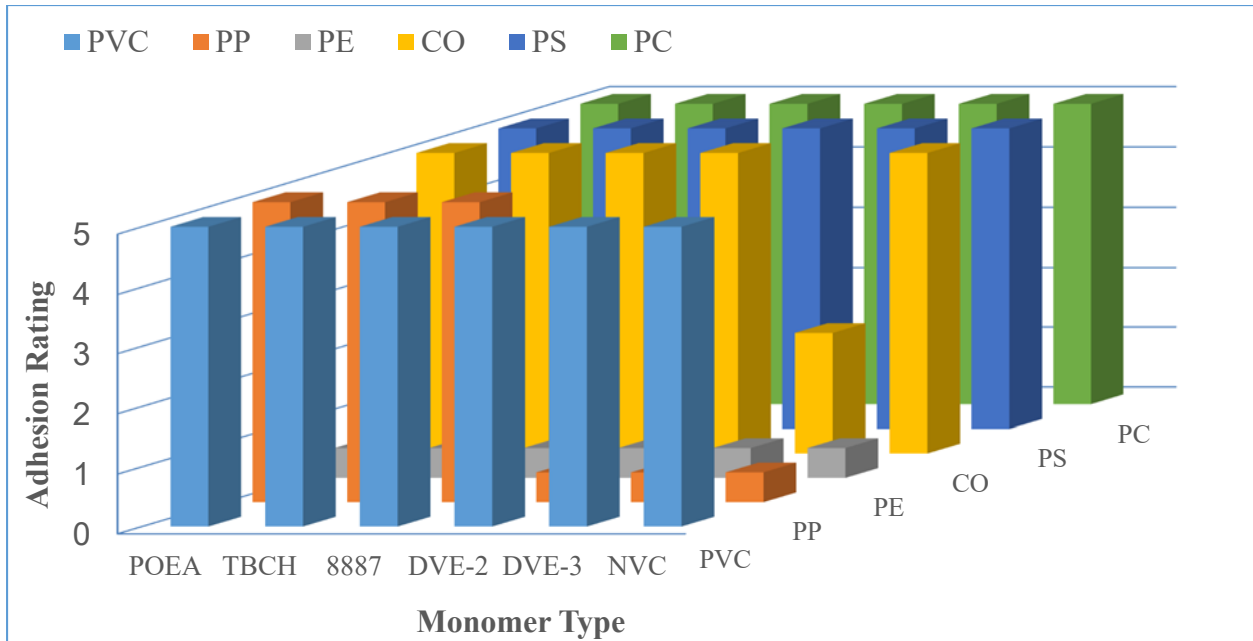


Figure 6. Cured ink adhesion over substrates containing mono acrylates and vinyl ethers

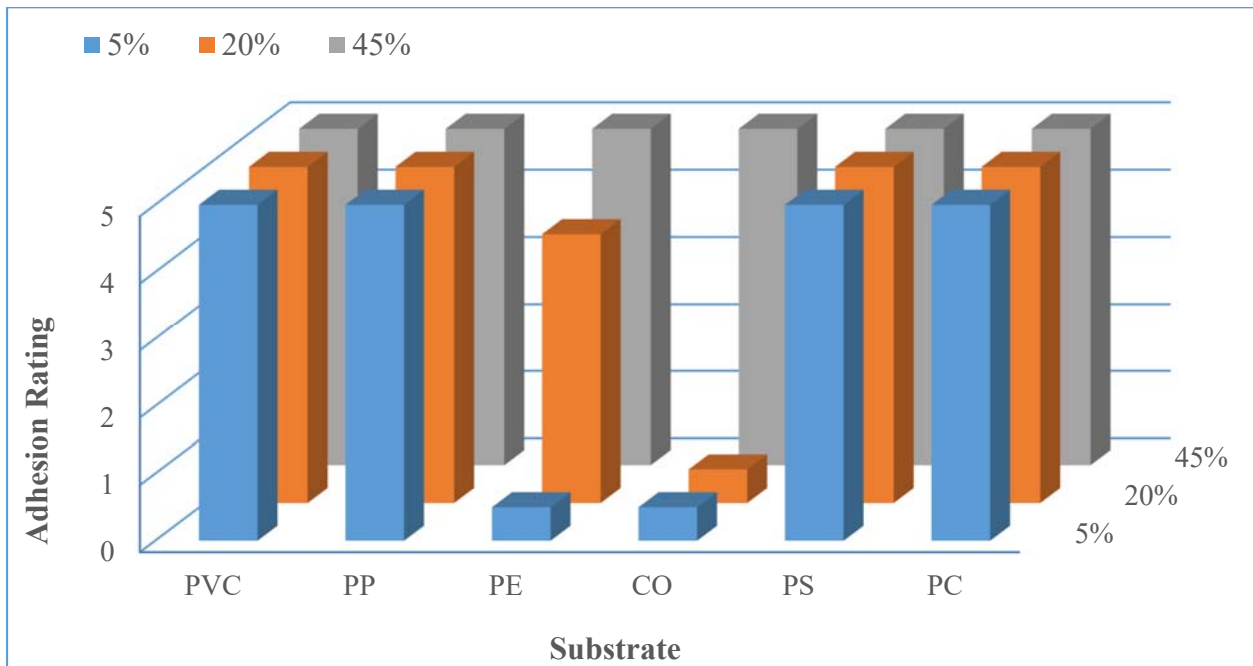


Figure 7. Cured ink adhesion over plastic substrates with increasing amounts of NVC

3.3 Statistical Design of Experiment (DoE) to optimize photoinitiator package

Due to migration and residual color issues in clear coatings related to ITX, a photosensitizer, we also wanted to investigate if Irgacure® 500 could be used instead of ITX in application involving printing and packaging. Furthermore, the type, level and relative ratios of photoinitiators chosen

is key in achieving material properties and speed. A Statistical Design of Experiments (DoE) was performed in order to optimize the PI package. A DoE systematically varies components, such that interactions can be identified; and essentially builds a mathematical model of the formulation. The design shown in Table 4 was based on formulation from Table 3, by keeping Irgacure® 500 at a fixed level of 2%. Appropriate ranges for Irgacure 819, LEX-201 and Irgacure 127 were chosen and constrained such that the total for these three components was 13%. Levels for the components were: Irgacure 819 from 1 to 4%, LEX-201 from 4 – 10% and Irgacure 127 from 1 – 5%. Formulations were made by dissolving photoinitiators in a mixture made prior by using all the fixed components of the design. A partial cubic mixture design was chosen. We measured the following responses in the finished ink: viscosity, cure speed, chemical resistance and adhesion over polycarbonate, biaxial oriented polypropylene and polyvinyl chloride substrate. The partial cubic mixture design gave us the information on an optimized photoinitiator package that imparts fast cure speed. From this design we chose to optimize the formulation by attempting to determine which formulation provided acceptable performance at the lowest level of UV exposure.

| Sample # | 45-1 | 45-2 | 45-3 | 45-4 | 45-5 | 45-6 | 45-7 | 45-8 | 45-9 | 45-10 | 45-11 | 45-12 | 45-13 | 45-14 | 45-15 | 45-16 | 45-17 | 45-18 | 45-19 | 45-20 |
|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| Trial | 15 | 5 | 1 | 9 | 3 | 5 | 13 | 1 | 4 | 2 | 14 | 2 | 11 | 6 | 12 | 10 | 7 | 8 | 4 | 3 |
| Irgacure 819 | 2.50 | 1.83 | 4.00 | 3.17 | 1.00 | 1.83 | 4.00 | 4.00 | 2.55 | 2.00 | 1.00 | 2.00 | 1.00 | 1.00 | 4.00 | 3.33 | 3.00 | 4.00 | 2.55 | 1.00 |
| LEX 201 | 5.50 | 7.28 | 4.00 | 4.83 | 7.00 | 7.28 | 8.00 | 4.00 | 8.34 | 10.00 | 9.17 | 10.00 | 7.83 | 10.00 | 5.11 | 6.34 | 9.00 | 6.89 | 8.34 | 7.00 |
| Irgacure 127 | 5.00 | 3.89 | 5.00 | 5.00 | 5.00 | 3.89 | 1.00 | 5.00 | 2.11 | 1.00 | 2.83 | 1.00 | 4.17 | 2.00 | 3.89 | 3.33 | 1.00 | 2.11 | 2.11 | 5.00 |
| Mixture | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 | 87.00 |
| HDDA | | | | | | | | | | | | | | | | | | | | |
| TPGDA | | | | | | | | | | | | | | | | | | | | |
| V-CAP | | | | | | | | | | | | | | | | | | | | |
| POEA | | | | | | | | | | | | | | | | | | | | |
| Urethane Oligomer | | | | | | | | | | | | | | | | | | | | |
| AA-4 | | | | | | | | | | | | | | | | | | | | |
| Stabilizer | | | | | | | | | | | | | | | | | | | | |
| Irgacure 500 | | | | | | | | | | | | | | | | | | | | |
| Wetting Agent | | | | | | | | | | | | | | | | | | | | |
| Viscosity (CPS), 1667 s ⁻¹ | 22.3 | 22.9 | 20.9 | 21.6 | 23.2 | 23.6 | 23.5 | 21.6 | 23.5 | 24.8 | 23.1 | 24.8 | 22.6 | 23.3 | 22.2 | 22.6 | 24.2 | 22.5 | 24 | 23.6 |
| MEK Rubs Test: | | | | | | | | | | | | | | | | | | | | |
| PVC | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Polypropylene (BOPP) | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Polycarbonate | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| X-Hatch Adhesion | | | | | | | | | | | | | | | | | | | | |
| PVC Gloss (NEW) | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B |
| Polypropylene (BOPP) | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B |
| Polycarbonate | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B | 5B |
| Cure Speed | | | | | | | | | | | | | | | | | | | | |
| 1/Exposure | 8.33 | 6.13 | 11.24 | 8.06 | 5.71 | 5.88 | 8.40 | 8.00 | 6.02 | 3.60 | 3.44 | 4.88 | 4.69 | 2.19 | 4.88 | 7.69 | 5.62 | 7.63 | 5.65 | 4.85 |

Table 4. DoE formulations containing low migration photoinitiators

We subsequently performed confirmation tests to ensure the model was predicting as expected. Data obtained was within the error associated with the response; in other words, the model was doing as good a job as we could expect given the replicate standard deviation in the design. Based on the results, we did not see much variation on the viscosity and material properties from the design. Effect on the cure speed was much more apparent based on the levels of photoinitiators used in these formulas. A significantly high level of Irgacure 127 and lower level of LEX-201 in the design was found to impart fastest cure speed without much effect on viscosity and material

properties. We identified the formulation based on this optimization and an example of starting point formula is shown in Table 5 along with the material properties.

| Materials | Amount |
|--|---------------------|
| Urethane Oligomer | 4 |
| HDDA | 39.9 |
| NVC | 10 |
| POEA | 10 |
| AA-4 | 5 |
| TPGDA | 15 |
| Irgacure 819 | 2.7 |
| Irgacure LEX-201 | 5.3 |
| Irgacure 127 | 5 |
| Irgacure 500 | 2 |
| Efka SL 3257 | 0.1 |
| Irgastab UV 22 | 1 |
| Total | 100 |
| η (cps) @ 25C, 1667 Sec ⁻¹ | 21.9 |
| 1/Exposure (cm ² /mJ) | 8.2 |
| Belt Speed (FPM) | 62 |
| % Power | 40 |
| PVC, Polypropylene, Polycarbonate | > 100 MEK Rubs |
| PVC, Polypropylene, Polycarbonate | 5B X-hatch Adhesion |

Table 5. Optimized clear ink formulation containing low migration photoinitiators

4. Conclusions

Based on this study on clear jettable OPV's, we find that polyether amino acrylate AA-4 provides very good cure properties. Also, the use of N-vinyl caprolactam enables adhesion over wide variety of plastic substrates. Furthermore, we also find that the use of low migration photoinitiators in inks enables very good cure speed and material properties. These formulas were all derived from polyurethane acrylates and will be the subject of further study in pigmented inks.

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References

[1] Le, H.P., Journal of Imaging Science and Technology, 42, Number 1, January/February, (1998).

[2] R Schwalm, J Baro RadTech Europe Conference & Exhibition 15 - 17 October 2013 Basel/Switzerland.

[3] Laromer[®], Irgacure[®], Efka[®] and Irgastab[®], are trademarks of BASF Group.

[4] E. V. Sitzmann, “Critical photoinitiators for UV-LED Curing: Enabling 3D Printing, Inks and Coatings“, RadTech UVEB West 2015, Redondo Beach, CA.

[5] E. V. Sitzmann., J Kaczun., "New dual function resin with initiator and acrylate functionality for low migration applications”. RadTech UV/EB 2014, May 12-18, 2014 Chicago, IL.

[6] R. Balmer, T. Newsom, G. Shouldice, “Advances in Printing Inks for Alternative UV Sources”, NPIRI Technical Conference 2013.

[7] E.V. Sitzmann, K. Davidson, A. Bendo and P. Vanvolsum, “Photoinitiator selection strategies for thick section curing of composites and adhesives” RadTech UVEB West 2007, Los Angeles, CA

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