Reactive Inkjet Formulations - Curing By Electron Beam

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Abstract

Ultraviolet light (UV) reactive inkjet printing has become well known as a reliable printing method for graphic display printed products . Single pass UV-curing inkjet printing systems are now becoming technically feasible, where sheets or a web are printed when passing under a static array of printheads. An area of interest for UV inkjet is indirect contact food packaging, but UV inkjet inks are less than ideal.

The energy of a typical UV photon is below the chemical bond energy of acrylate monomers; this means that the curing reaction cannot be initiated without the presence of a photoinitiator. As the energy of electron beam (EB) electrons easily exceeds the bond energy of acrylate monomers, they will initiate cure without added photoinitiator. Problems of migration, taint, and odour associated with uncured photoinitiator and photoinitiator fragments are then eliminated.

EB curing of reactive inks is well known for offset and flexography indirect food packaging printing, as there is potential for low migration. There is therefore a strong driver to extend this curing process to ink jet systems.

In this paper the concept of combining EB as the cure method and inkjet as the printing method is discussed, with the objective of printing indirect contact food packaging. The paper focuses on aspects of the formulation of photoinitiator free reactive inkjet inks, including monomer selection and type and the effect this has on migration levels when cured by an electron beam process.

Introduction

The use of reactive inkjet technology has become a major factor in the printing of variable image and short run graphic display products. This is because the inks do not dry in the nozzles , they have good adhesion to non-porous substrates and they do not have high volatile organic solvent emissions. However, all of the applications use ultraviolet (UV) light as the curing mechanism. UV-curing is a good technology for scanning print heads, where the lamps are attached to the print head, and need to be relatively light for the acceleration and deceleration they experience.

More recently, single pass UV-curing machines have been developed, where the print-heads are connected together to span the full width of the substrate. Here lamps are stationary, with the web or sheets passing through at speed, printing in just one pass. An example of a sheet fed machine is SunChemical's Fastjet ™ printer which prints corrugated cardboard packaging and an example of a web fed machine is Agfa-Dotrix's Modular digital press. (Figure 1)

Figure 1. Agfa-Dotrix's Modular digital press.

The type of chemistry which has predominated in reactive inkjet inks is UV reactive free radical chemistry. After printing there is a cure stage, where photoinitiators (PI's) interact with UV light to form free-radicals which then attack double bonds in the acrylate monomers, creating a coloured image polymeric coating.

Within the market area of food packaging, single pass energy curing inkjet can suit the creation of the graphic where short runs are required, or there are advantages in eliminating time taken for image change over; or to avoid the need to hold printed stock ('Point of fill ' printing). Thus the overall print cost can be lower than conventional flexography or gravure printing. These advantages also apply to the printing of pharmaceutical packaging.

However, for UV-curing a photoinitiator is required, as the energy of a typical UV photon is below the chemical bond energy of acrylate monomers and so cannot cleave these bonds to form radicals directly. [1]

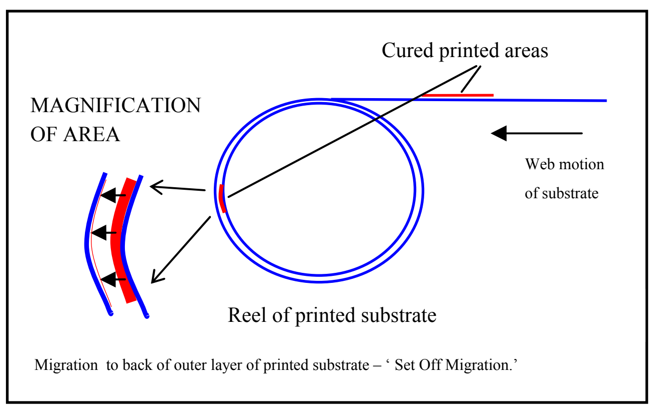


Figure 2. ' Set Off Migration ' - Process of potential migration onto side of packaging which later forms interior of container for food product.

The disadvantage with this situation is that the photoinitiators and the fragments they break down into are typically small molecules which are prone to migration. Although the ink is on the outside of the packaging, if the printed substrate is re-reeled a ' set off migration ' can occur, which would put migratables in contact with the food.(Figure 2.)

Secondary migration can then occur of the migrated PI's into the food once the container is formed, in Europe the level of migration considered acceptable is controlled by EU legislation and industry agreement and is low, typically between <50ppb and <10 ppb being allowed, when measured in a simulated ' set off ' migration test. [2 , 3]

Innovations have been made to reduce the migration of PI's. Some work describes the use of multifunctional photoinitiators, where the statistical probability of at least one radical curing into the polymer matrix is increased, thereby making it immobile, and preventing migration [4]. In other work the photoinitiators themselves have a polymeric part, with a significantly higher molecular weight, and lower mobility. However, both of these approaches reduce the weight for weight active functionality of the PI, and hence the reactivity, cure speed, and thus printing speed achievable.

If it was possible to cure a reactive inkjet ink without photoinitiators it would be advantageous, as no migration would occur from these components. As the energy of electron beam (EB) electrons easily exceeds the bond energy of the bonds in acrylate monomers, they can form radicals at sites on the monomer, and will initiate cure without photoinitiator. Problems of migration, taint and odour, associated with uncured photoinitiator and photoinitiator fragments are thus eliminated.

EB-curing of more viscous reactive inks is well known in offset printing, and to some extent flexographic printing (for example SunChemical – Sunbeam ™ and Wetflex ™ inks respectively). These inks have potential to be used in indirect food packaging printing as they can have low migration, but do not have the advantages of variable image and instant change over of an inkjet process. The cost of EB units has dropped to between 45% to 65 % of their cost 9 years ago, also making their use more economically viable.

Therefore the combination of single pass inkjet printing, with photoinitiator free reactive inkjet inks, and electron beam curing, is an attractive way of printing indirect contact food packaging.

$$\underset{\text{ORGANIC MOLECULE}}{XY} + e^-_{kin} \rightarrow XY^{+}\bullet + e^- + e^-_{kin}$$

$$XY^{+}\bullet \rightarrow \underset{\text{RADICAL}}{X\bullet} + \underset{\text{CATION}}{Y^+}$$

Figure 3. Equation for generation of radical by electron bombardment of an organic molecule (XY)

However, another species of potential migrant needs to be considered in such a situation. The nature of the inkjet process is such that it requires low viscosity (approx 30cP at room temperature,) and to obtain this acrylate monomers (rather than acrylate oligomers) must be used. These relatively small, lower molecular weight molecules can themselves migrate, so their selection needs to be carefully controlled. In this paper, aspects of the reactivity of the monomers, and the dose used are investigated, looking at the effect these factors have on migration levels.

The Electron Beam Curing Process

Figure 3 shows a possible mechanism for the creation of radicals from the high energy electrons [5], though other mechanisms may occur. Figure 4 shows a diagram of an EB cure unit, it is one which is suitable for curing ink on a printed web. In an electron beam curing unit, electrons are produced from a filament, then accelerated through a vacuum, and pass through a foil window to exit the generation area. The beam then travels across a gap before passing into an ink layer on the carrying substrate. Here the electrons may generate a free radical. This radical will then attack the double bonds in the acrylate monomer, as discussed previously. Lead shielding is present to trap X-rays which may also be generated.

The presence of oxygen above and in the film can consume the radicals created, therefore a layer of inert gas, usually nitrogen, is present in the curing area of the machine. This replaces the oxygen, and prevents the radicals being quenched.

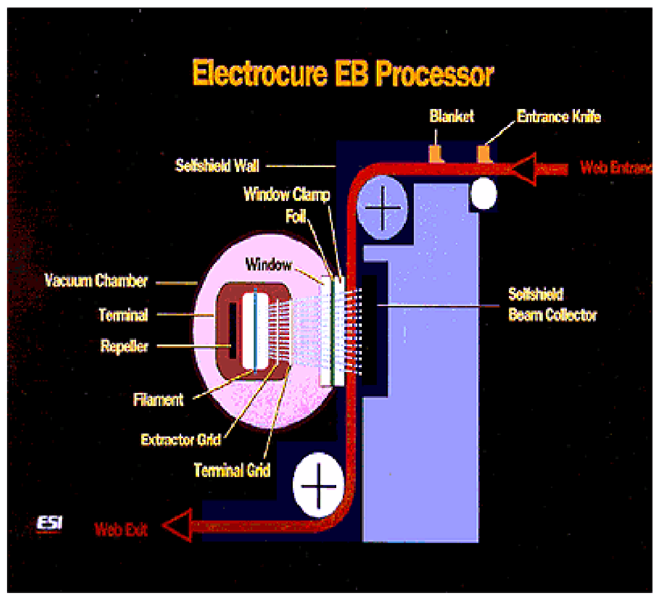
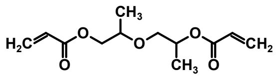


Figure 4. Schematic of parts of an EB cure unit. Courtesy of ESI.

Experimental

Ink formulations

Key free radical monomers were identified, and combined in photoinitiator free inkjet formulations. The monomer dipropylene glycol diacrylate (DPGDA) was used as a main constituent for the formulations (65%), as it's presence can easily be detected by gas chromatography mass spectrometry(GCMS).



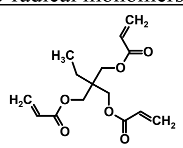
Dipropylene glycol diacrylate

A SunChemical magenta pigment dispersion (of a proprietary composition) was also used in each formulation giving a level of 2.1% pigment in the test ink.

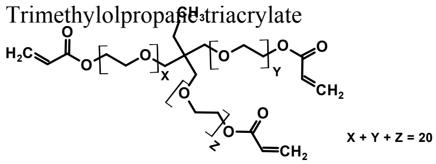
Level of EO / PO of Monomers

It is known that the presence of easily ionized groups such as ethers can promote the formation of radicals in an EB system. An investigation was made to assess the effect of this on migration. The number of ethoxy- and propoxy- groups was varied on a trimethylpropane triacrylate base molecule. This was achieved by obtaining commercially available monomer samples from Sartomer, Rahn, Cognis and AGI. Ethoxylation levels of 0, 3, 7, 9, 14 and 20 units , and propoxylation levels of 0, 3 and 6 units were obtained. 25% of the relevant ethoxy / propoxy material was combined with DPGDA in each formulation, and 5% dipentaerithritol hexaacrylate was also added to each, to improve film properties and reactivity.

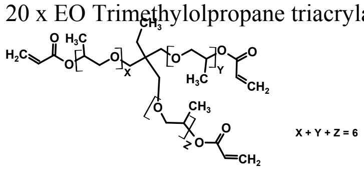
<u>Free-radical monomers – from Sartomer, Rahn, Cognis and AGI</u>



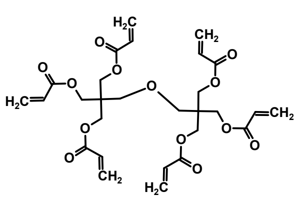
Trimethylolpropane triacrylate



20 x EO Trimethylolpropane triacrylate



6 x PO Trimethylolpropane triacrylate



Dipentaerithritol hexa-acrylate

Level of Dose Of Electron Beam Energy

The effect of the level of dose was assessed on the 20 x ethoxylation TPMTA formulation from the previous experiment. The dose given by the EB cure unit was increased from 5 to 45 kGy in 5kGy steps.

Curing and Migration Testing

The formulations were coated using a 12µm K-bar on Leneta card substrate. They were then cured with an AEB electron beam lab curing unit. The cure conditions for the first experiment were a dose of 30 kGy, an electron accelerating voltage of 110kV, and nitrogen inerting to achieve < 2ppm oxygen level. The line speed was 30m / minute. In the second all settings were identical, except that the dose was varied, as stated previously.

A test of the 'set off migration ' from the DPGDA monomer was then conducted. The cured prints (100cm^2) were stacked in contact with polyethylene (PE) with the untreated side of the PE substrate in contact with the ink (PE from Schur Plastic).A SPECAC hydraulic press then applied 10 tonnes of pressure for 24 hours (to replicate any ' set off migration' that might occur). An inert barrier layer (aluminium foil), was placed between each set of migration tests to prevent cross contamination. After 24 hours the polyethylene films were placed individually in migration cells, and 100mls of ethanol was added to each cell. The cells were stored for 24 hours at room temperature. After storage the ethanol was decanted, concentrated by evaporation and analysed using GC-MS(to simulate movement of migratables into a food or drink).

The results were reported in ppb, which is the equivalent of µg/kg food, calculated according to the EU model, where 1 kilogramme of food is assumed to be wrapped by 600cm^2 of substrate.

Results- Level of EO / PO of monomer

All formulations had viscosities which were within the range for successful printing in a piezo DOD inkjet head.(8 to 12 cP @ 40-55C) All cured to a tough film on the substrate. The effect of the ethoxylation level of the TMPTA used on the level of 'set off migration ' of DPGDA is shown in Figure 5. Here it can be seen that as the level of ethoxylation is increased, the level of migration of the DPGDA is reduced. It appears that the increase in the level of these easily ionized groups achieves reduced migration in formulations of ink jet viscosity. This is an effective way to reduce the migration. It is believed to work by increasing the number of radical species generated, which increases the proportion of DPGDA groups which react into the polymer matrix which develops, reducing the amount free to migrate out of the cured film. The results suggest that there is some reduction in the efficiency of adding more EO groups after approximately 8 EO units, when the rate of reduction of migratables which this achieves reduces.

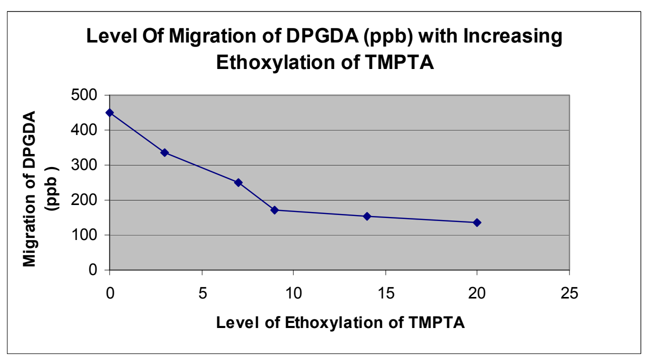


Figure 5. Level of migration of DPGDA with increasing ethoxylation of TMPTA

The effect of the propoxylation level of the TMPTA used on the level of ‘set off migration ’ of DPGDA is shown in Figure 6. Here it can be seen that as the level of propoxylation is increased, the level of migration of the DPGDA is reduced. It can also be seen from these results that for the same proportion by weight, propoxylation gave a greater reduction in migration of DPGDA than ethoxylation. It is interesting to note that this effect , which is known in the industry , also occurs at inkjet viscosities.

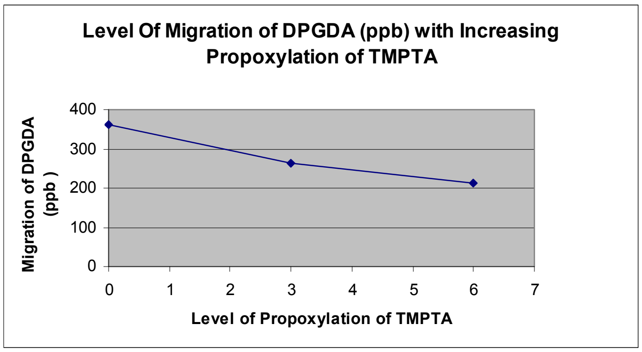


Figure 6. Level of migration of DPGDA with increasing propoxylation of TPMTA

Results – Level of dose of EB energy

The effect of increasing the dose of EB energy is shown in Figure 7. Here the results show that low doses give high levels of ‘ set off migratables’. At high doses the level of DPGDA migratables approaches the level required in Europe. This is because higher doses give higher radical densities for more cure.

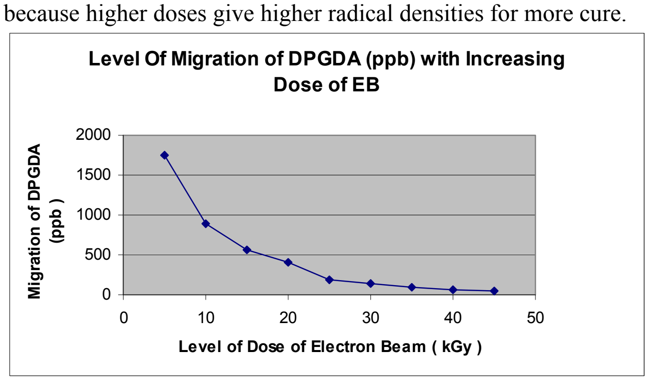


Figure 7. Level of migration of DPGDA with increased dose of EB energy.

Summary

Results have shown that careful selection of ethoxylated and propoxylated monomers can reduce ‘set off migration ’, even at the low viscosities used in inkjet printing. Propoxylation appears to achieve lower levels of migratables than ethoxylation for the same number of repeat units. The use of higher doses of electron beam energy on an ethoxylated acrylate monomer allow migration levels which are low enough to approach the legislative requirements for ‘set off migration ’ for indirect food packaging printing in Europe.

This approach is enabling in the use of reactive inkjet technology for printing indirect food packaging, as it allows the advantages of a digital system combined with the low migration required.

References

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[3] EuPIA Guideline on Printing Inks applied on the non-food contact surface of food packaging materials and articles – July 2006, pg6.
[4] S. Herlihy , The use of Multifunctional Photoinitiators to Achieve Low Migration in UV Cured Printing Applications, Conference Proceedings Radtech US, pg143 (2002)
[5] G Webster, Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints .Vol. II. 1997 pg17

Author Biography

Hartley is Research Manager at SunJet, Bath, UK, the R&D headquarters of the inkjet division of SunChemical, where he is responsible for new technology development. This followed his position of UV Inkjet Project Leader, at SunJet. In this role he developed a wide range of UV curing inkjet technologies for graphic arts and other applications over a 10 year period. He has a BSc (Hons) from the Open University and holds several patents in UV inkjet formulation.

Steve graduated from Bath University with a 2(i) Hons Degree in chemistry in 1983. He then joined Cray Valley where he progresed to Technical Manager, Electronic Resins. In 2003 he moved to SunChemical and in 2008, on the promotion of Hartley Selman, he took over the position of Project Leader for the development of UV Jet Inks at SunJet, Bath