Bisphenol A Free Resin Options for Inks and Overprint Varnishes

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ABSTRACT

The August 2016 Nestle Guidance Note on Packaging Inks states that "Bisphenol A (BPA) and materials manufactured from or incorporating BPA in reacted form as part of the chemical structure must not be used." Many energy curable inks and overprint varnishes (OPVs) contain bisphenol A epoxy acrylates, polyester acrylates that may be based on bisphenol A, and/or ethoxylated bisphenol A diacrylate. In order to meet the Nestle requirements for food packaging, alternatives to these bisphenol A based materials are needed. These alternative materials must not only meet food packaging requirements, they must also maintain the performance properties of the ink or OPV, and provide economics in use. This paper will review the bisphenol A free resin options that are available to the ink or OPV formulator.

BISPHENOL A

Bisphenol A is a xenoestrogen (estrogen mimic), and as such, was and is under scientific scrutiny. However, the science around the safety of bisphenol A in food packaging has become largely irrelevant, as the consumer has abandoned products containing BPA. Today, many brand owners, including Nestle and IKEA, no longer want BPA in their products or packaging. In order to prevent ambiguities in measurements and detection limits, Nestle revised its Guidance Note in 2016 to read "Bisphenol A (BPA) and materials manufactured from or incorporating BPA in reacted form as part of the chemical structure must not be used." Figure 1 shows the structural similarities of estradiol (most common estrogen) and bisphenol A.

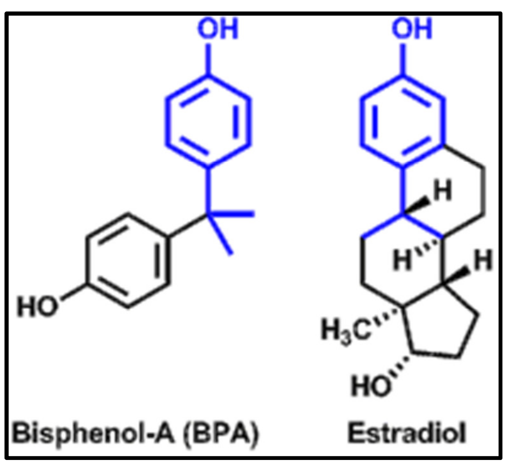

Figure 1. Structural Similarities of BPA and Estradiol

BISPHENOL A DERIVATIVES & PROPERTIES

The 2016 Nestle Guidance Note on Packaging Inks precludes the use of materials derived from bisphenol A. Some of these derived materials are alkoxylated bisphenol A, hydrogenated bisphenol A, and bisphenol A diglycidyl ether. Polyester acrylates and epoxy acrylates based on these products are also banned. Bisphenol A epoxy acrylates are widely used in energy curable overprint varnishes (OPVs) and inks in food packaging applications. Figure 2 shows the synthetic scheme for the BPA epoxy acrylate. Modifications can be made to the synthetic scheme to make more flexible, faster curing, better pigment wetting, or lower viscosity epoxy acrylates, but the bisphenol A structure remains in all of these modified materials.

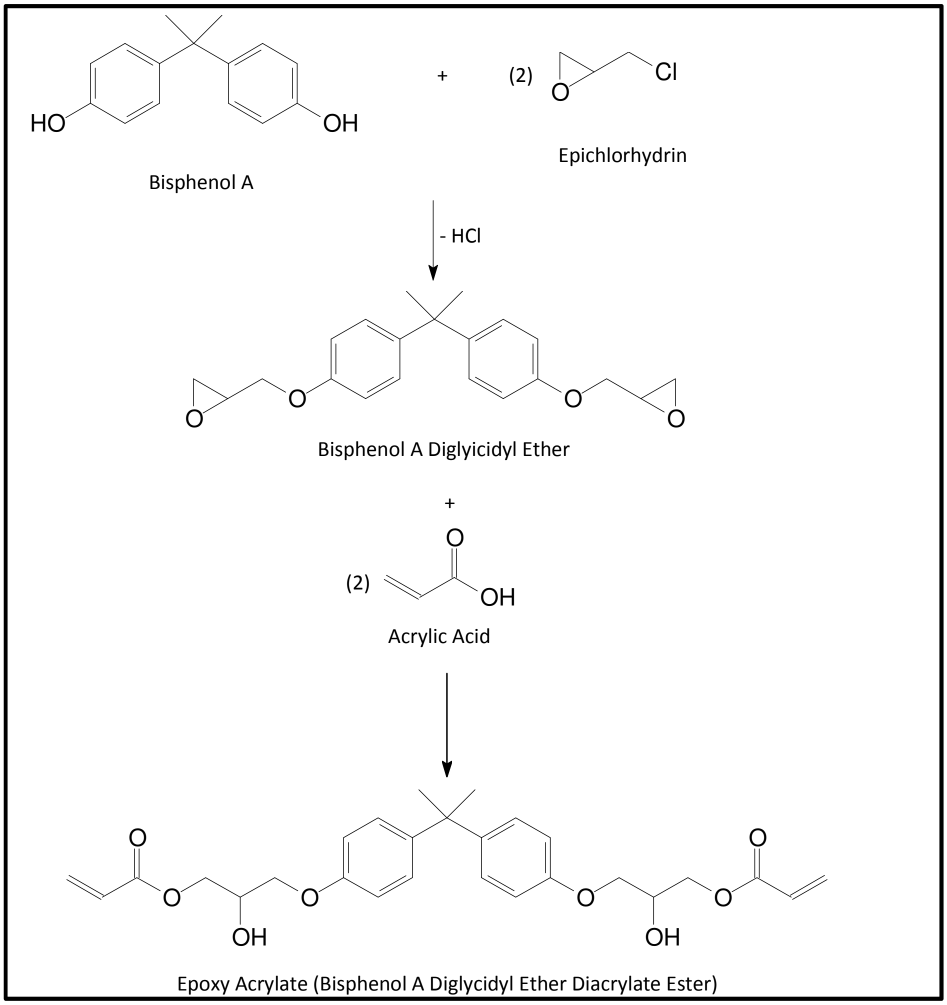

Figure 2. Synthetic Scheme for the Production of BPA Epoxy Acrylate

Structurally, the BPA epoxy acrylate has aromatic rings, hydroxyl groups, double bonds, and low molecular weight (~525). The hydroxyl groups participate in hydrogen bonding, resulting in very high viscosity at room temperature (~1,000,000 cP), and a steep viscosity-temperature curve. Monomer dilution curves are also typically steep. Cure speeds of formulations containing epoxy acrylates are generally fast, and cured inks and coatings are hard, chemical resistant, and glossy. Cured films with high tensile strength and modulus, but low elongation are also obtained. The price of epoxy acrylates, as a class, has always been comparatively the lowest. Table 1 summarizes the properties of bisphenol A based epoxy acrylates.

Table 1. Properties of Bisphenol A Based Epoxy Acrylates

Structural Properties	Uncured & Cured Properties
Aromatic Rings	High Viscosity
Hydroxyl Groups	Fast Cure
Hydrogen Bonding	Hardness
Low Molecular Weight	Chemical Resistance
Double Bonds	High Gloss
	High Tensile Strength & Modulus
Low Price	Low Elongation

OPVs AND INKS BASED ON BPA EPOXY ACRYLATES

Especially because of cure speed, gloss, and price, overprint varnishes were almost always based on BPA epoxy acrylates. Table 2 shows the formulation of a basic OPV. Because of the high viscosity of BPA epoxy acrylate, a large amount of monomer can be used to reach the desired OPV viscosity range of 300-500 cP. This provides a cost benefit to the OPV. Most of the other, more specialized OPVs were also based on BPA epoxy acrylates. Some examples are OPVs for multi-wall bags, chemical resistant and flexible OPVs, OPVs for wax based substrates, and OPVs over water based flexo inks, or for wet trapping oil based litho inks.

Many energy curable inks (flexo, litho, screen) use some BPA epoxy acrylates or modified BPA epoxy acrylates in their formulations. These can be used for better adhesion, increased resistance properties, faster cure speed, and/or tack adjustment. Replacing BPA based materials in these applications can be more complicated than replacing those for OPVs.

Table 2. Basic OPV Formulation Based on BPA Epoxy Acrylate

Component	Parts
Epoxy Acrylate	15
TMPTA (trimethylolpropane triacrylate)	10
TMPEOTA (ethoxylated trimethylolpropane triacrylate)	60
Photoinitiator (benzophenone)	5
Amine	6
Photoinitiator (2-Hydroxy-2-methyl-1-phenyl-propan-1-one)	4
Silicone Acrylate	0.5
Viscosity (cP, 25°C)	**300-500**

NESTLE LIST REQUIREMENTS & RESTRICTIONS

Besides banning the use of bisphenol A in food packaging applications, Nestle also bans the use of many photoinitiators, including the two shown in Table 2. TMPTA is also on the

Nestle "minimize" list, which means it can only be used in an amount, if any, necessary to achieve the desired properties. Not only are the Nestle banned and minimize lists important, the final, converted product must meet the requirements for migration into food. The Specific Migration Limits (SMLs) shown in the Swiss List must be met. (The Nestle List is an exclusion list based upon the Swiss List.) SMLs for migrating species are either based on toxicological evaluations (Part A) or default to 10 ppb if not yet evaluated (Part B).

To limit migrating species, special care should be taken in both the selection of raw materials and the manufacturing process. Raw materials should be of a certain purity, and also not contain CMRs (carcinogens, mutagens, reprotoxins). Cross contamination during processing should be avoided through proper planning, or through full GMP (good manufacturing practice). A purification step may also be needed to remove migrating species. Quality control (QC) may also have purity/cross contamination specifications. Table 3 shows the differences between standard products, low migration (LM) products, and full GMP products. Low migration and full GMP products should be, by design, Swiss and Nestle List compliant.

Table 3. Differences Between Standard, Low Migration, and GMP Products

	Standard	Low Migration	Full GMP
Raw Material Selection	Technical Performance	Technical Performance	Technical Performance
	Cost	No CMR	No CMR
		Cost	Purity
			Cost
Production	ISO 9001	ISO 9001	ISO 9001
		Purification Step	Purification Step
			GMP
QC	Physico-Chemical	Physico-Chemical	Physico-Chemical
			Impurities
			GC-FID/MS

Another way to limit migrating species, is through the use of multifunctional materials (>/= 3 functional), and high molecular weight materials. Higher functionality increases the probability that at least one double bond reacts into the polymer backbone. If one double bond reacts, the material becomes part of the polymer backbone, and cannot migrate. Higher molecular weights also help limit migration, as these materials can become entangled in the polymer backbone, as well as react through their double bonds. Migration also becomes more difficult as molecular weight increases.

As has been discussed in this section, formulating an OPV or ink for Nestle compliance requires a good understanding of the regulations, and multiple material options.

OPTIONS TO REPLACE BPA EPOXY ACRYLATES

There are four general classes of energy curable oligomers: epoxy acrylates, polyester/polyether acrylates, urethane acrylates, and amino acrylates. Diluting acrylates, or acrylated monomers, are used to reduce the viscosity of the oligomers. These classes will be reviewed for their potential to replace BPA epoxy acrylates.

Since bisphenol A is an estrogen mimic, using structurally similar materials like bisphenol F is not considered as a solution. Other potential epoxy acrylates would include acrylated epoxidized oils, such as soya or linseed oil. In general, these oil based materials have much decreased properties compared to bisphenol A based epoxy acrylates, are lower in viscosity, and are more expensive. They do have good pigment wetting, however. Acrylated epoxy novolacs have good resistance properties and high viscosity, but may contain residual bisphenol F and/or formaldehyde. The acrylated aliphatic epoxy resins tend to have toxicity issues, and are generally not suitable for food packaging.

Polyester/polyether acrylates are a potential replacement for epoxy acrylates. However, this class of materials in general, is more expensive, lower in viscosity, and lower in resistance properties. There are exceptions, however, as a wide variety of structures are possible within this class of materials. Good pigment wetting is a plus for many of the polyester acrylates.

Urethane acrylates have a wide variety of functionalities, dilutions, and properties. They can provide excellent properties, such as hardness and resistance properties, or flexibility and toughness. The major drawback for this class of materials is high cost, and lack of suitability as base materials for inks.

Amino acrylates are fast curing and low viscosity. As modifiers, they can provide fast cure speeds in OPVs. They are generally not suitable for inks, especially litho inks. They are also more expensive than epoxy acrylates.

The diluting acrylates, as a class, are low viscosity materials that can be used in combination with other oligomer classes to obtain target viscosities. They can increase cure speed and some resistance properties.

A rather new class of oligomers is waterbased energy curable polyurethane dispersions (EC PUDs). These materials are generally high molecular weight and multifunctional. They use water as a diluent instead of acrylated monomers, and are very low viscosity (< 200 cP). These characteristics make them extremely interesting for food packaging applications for the reasons discussed earlier. With this technology, the water must be evaporated, and the EC PUD allowed to coalesce before the curing process. This may require equipment modification or new equipment design.

Reviewing this brief look at oligomer classes, it seems that there will be few materials, if any that can be used as a one-to-one replacement for the BPA epoxy acrylate. Either reformulation or new oligomer design will be needed to effectively replace BPA epoxy acrylates in OPVs and inks. Several approaches to BPA free OPVs and inks will follow.

NESTLE/SWISS LIST COMPLIANT FORMULATIONS FOR OPVs AND INKS

A new polyester acrylate (PEA X) has been developed for use in OPVs. This material is a one-to-one replacement for the 40% TMPTA dilution of epoxy acrylate. Table 4 shows the properties of this material compared to the epoxy acrylate. The formulation is Nestle/Swiss List compliant, using only approved monomers and photoinitiators. The viscosities of the neat oligomers and the formulations are very similar, and the cured film properties (cure speed, gloss, chemical and scratch resistance) are the same. The cost structures of the two formulations are also very similar.

Table 4. One-to-One BPA Free Replacement for Epoxy Acrylate/40% TMPTA in OPVs

	EPOXY ACRYLATE 40% TMPTA	POLYESTER ACRYLATE X
Oligomer Viscosity	7100	8800
Formulation Components		
Oligomer	25	25
TMPEOTA	55	55
Photoinitiator (GMP Self Curing Resin)	20	20
Total	100	100
Viscosity (cP at 25°C)	492	451
Max Surface Cure Speed (fpm)	100	100
Energy Density (mJ/cm^2)	158	158
20° Gloss (3 x 100 fpm)	86	86
MEK DR (3 x 100 fpm)	>200	>200
Scratch Resistance (3 x 100 fpm; 6-layer cheese cloth, 1 kg hammer)	>100	>100

If a drop-in replacement is not required, several polyester acrylates, in combination with diluting acrylates and/or amino acrylates, can be used to formulate BPA free OPVs. Table 5 provides the details of the formulations, and the cured OPV properties versus that of an epoxy acrylate based OPV. In all cases, less TMPEOTA is required to obtain the same viscosity as the epoxy acrylate based formulation. This will generally result in a more expensive formulated cost. Polyester Acrylate 1 is less reactive than Polyester Acrylate 2 or 3, so both amine modified polyether acrylate and dipentaerythritol penta/hexa-acrylate (DPHA) are required in its formulation. The viscosities of the formulations range from 400-600 cP, and the refractive index of the aromatic epoxy acrylate formulation is higher. They all cure at least as fast as the epoxy acrylate formulation. Polyester Acrylate 2 is notable for its cure speed, which is twice that of the epoxy acrylate. Gloss values and solvent and scratch resistance are the same for all formulations.

Table 5. BPA Free Polyester Acrylate Based OPVs

Components				
Epoxy Acrylate	20			
Polyester Acrylate 1		22		
Polyester Acrylate 2			50	
Polyester Acrylate 3				30
Amine Modified Polyether Acrylate		10		
TMPEOTA	60	38	15	50
4 Functional Diluting Acrylate			15	
DPHA		10		
Photoinitiator (GMP Self Curing Resin)	20	20	20	20
Total	100	100	100	100
Viscosity (cP @ 25°C)	589	557	556	422
Refractive Index (20°C)	1.500	1.485	1.495	1.491
Applied with #2 bar, ~5 µm on uncoated Leneta chart				
Cured with 1 x 400 wpi Hg lamp				
Max Surface Cure Speed (fpm)	100	100	200	100
Energy Density (mJ/cm2)	158	158	81	158
20° Gloss (3 x 100 fpm)	89	84	87	86
MEK DR (3 x 100 fpm)	>200	>200	>200	>200
Scratch Resistance (3 x 100 fpm; 6-layer cheese cloth, 1 kg hammer)	>100	>100	>100	>100

In Table 6, an epoxy acrylate based OPV is compared to several amine modified polyether acrylate based OPVs. The viscosities of these materials are 450-600 cP, and again less TMPEOTA is required to obtain the same viscosity as the epoxy acrylate based formulation, resulting in higher formulation costs. The Amine Polyether 1 is faster curing than the other formulations, but also contains more of the five/six functional DPHA. The refractive index is again higher for the aromatic epoxy acrylate, and gloss values and solvent and scratch resistance are the same for all formulations.

Table 6. BPA Free Amine Modified Polyether Acrylate Based OPVs

Components				
Epoxy Acrylate	20			
Amine Polyether Acrylate 1		25		
Amine Polyether Acrylate 2			20	
Amine Polyether Acrylate 3				35
TMPEOTA	60	25	50	35
DPHA		30	10	10
Photoinitiator (GMP Self Curing Resin)	20	20	20	20
Total	100	100	100	100
Viscosity@25°C, cP	589	585	497	468
RI @20°C	1.500	1.486	1.485	1.487
Applied with #2 bar, ~5 µm on uncoated Leneta chart				
Cured with 1 x 400 wpi Hg lamp				
Max Surface Cure Speed (fpm)	100	125	100	100
Energy Density (mJ/cm2)	158	129	158	158
20° Gloss (3 x 100 fpm)	89	85	88	85
MEK DR, 3 x 100 fpm	>200	>200	>200	>200
Scratch Resistance (3 x 100 fpm; 6-layer cheese cloth, 1 kg hammer)	>100	>100	>100	>100

If a low migration, BPA free formulation is desired, low migration (LM) materials can be used to formulate the OPV. (See Table 7.) These LM materials are in the same classes as those products used in Tables 5 and 6, and can be expected to give similar OPV properties. For OPVs that need better adhesion, a low migration (LM) diluted polyester can replace the DPHA shown in Table 7.

Low migration flexo and litho inks can also be prepared using BPA free materials. Tables 8 and 9 show starting point formulations for these inks. LM black and white inks can also be prepared.

All of the solutions for BPA free OPVs and inks that have been discussed so far are 100% solids formulations. Waterbased energy curing materials can also provide a solution through the use of EC PUDs. Table 10 shows a variety of EC PUDs, their relative properties, and their recommended uses. The developmental products have been designed for low migration applications through raw material selection and adjustment of molecular weight and functionality. The resoluble materials can be used to formulate BPA free inkjet inks, as they will not clog the inkjet ink nozzles. For both OPVs and inks, formulations only involve the addition of additives, water and rheology modifiers for viscosity adjustment, pigments for inks, and photoinitiators for UV cure. The use of water for viscosity adjustment is a large benefit for low migration systems such as food packaging applications.

Table 7. Basic Food Packaging OPV Formulation Based on LM Materials

Component	Parts
LM Amine Modified Polyether Acrylate	50
LM 4-Functional Diluting Acrylate	28
LM Dipentaerythritol Penta/Hexa-acrylate (DPHA)	10
LM Polymeric Benzophenone Derivative	12

Table 8. LM Flexo Ink Starting Point Formulation

Component	Parts
PIGMENT PASTE	
LM Polyester Acrylate for Pigment Wetting; low viscosity	50 – 70
Dispersing Agent	4 - 10
Pigment	30 – 40
Stabilizer	0.1
INK	
Pigment Paste	35 – 45
LM Amine Modified Polyether Acrylate	0 - 25
GMP 3-functional Acrylated Diluent	15 - 35
Photoinitiator (GMP Self Curing Resin)	20 - 30

Table 9. LM Litho Ink Starting Point Formulation

Component	Parts
PIGMENT PASTE	
GMP Polyester Acrylate for Pigment Wetting	35
Filler	4 - 8
Pigment	14 - 20
Stabilizer	0.1
INK	
Pigment Paste	70 - 75
LM DPHA	20
Photoinitiator Blend	8 - 10

Table 10. Properties and Recommended Uses of EC PUDs

	Label-free	BPA-free	Tack-free	Resolu-bility	Migration	Reactivity	Flexibility
Commercial Products							
EC PUD 1	🟢	🟢	🔴	🟢	🟡	🟡	🟢
EC PUD 2	🟢	🟢	🔴	🟢	🟡	🟡	🟢
Developmental Products							
EXP 12	🟢	🟢	🟢	🔴	🟢🟡	🟡	🟢
EXP 29	🔴	🟢	🟢	🟢	🟢	🟢	🟡
EXP 53	🔴	🟢	🔴	🟢	🟢	🟡	🟢

🟢 Recommended Use 🟡 Fair Use 🔴 Not Recommended

CONCLUSIONS

In their 2016 Guidance Note, Nestle banned the use of bisphenol A (BPA) based products in food packaging. Many energy curable OPVs and inks for food packaging contain at least one product based on BPA. Reformulations of these OPVs and inks are needed, but it can be difficult to match their performance properties and also maintain their cost structures.

A new polyester acrylate (PEA X) has been introduced. PEA X is a drop-in replacement for epoxy acrylate diluted in 40% TMPTA. Formulations based on PEA X have essentially the same viscosity, cure speed, gloss, and chemical and scratch resistance as the epoxy acrylate based formulation. The cost structures of the two formulations are also very similar, making PEA X a very good option for BPA free OPVs for food packaging.

Other BPA free formulations for OPVs were introduced, but these were reformulations that have different cost structures versus the epoxy acrylate. The performance properties of these reformulations were the same as the epoxy acrylate, and in some cases, higher cure speeds were obtained.

Finally, BPA free starting point formulations for flexo and litho inks were presented, and the option to use waterbased energy curable PUDs in OPVs and inks was discussed.

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