Raw Materials for UV/EB Laminating Inks

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Abstract

UV/EB inks have traditionally been used in surface printing applications, but are now also being used as the inks in laminate structures. Within the laminate structures different interactions and forces act upon the ink and can influence the performance of the overall system. In this study the oligomer and monomer chemistry of the UV ink is varied and performance properties as a function of the raw material's properties are examined.

Introduction

As each year passes UV/EB technology further penetrates into established graphics markets and creates new markets as well. Traditionally UV/EB inks were used in surface printing jobs where the superior properties of the cured UV/EB inks led to improvements in solvent and abrasion resistance over solvent and water-based inks. The UV/EB inks also worked very well with the UV/EB coatings that were used in the packaging structure. Now printers are trying to use their UV/EB printing presses in new and more profitable areas. This has led the printers to start using UV/EB inks in laminated packaging structures.

Because of economics, the idea of using UV/EB inks inside of a laminate structure is new. Why would you pay for the performance of UV/EB inks if you were only going to put a protective film on top? There is a large installed base of UV flexo and UV and EB litho presses that currently run traditional print jobs. More profit lies in printing non-traditional jobs like shrink wrap and laminated packaging. This has led printers to then use their UV or EB presses in printing laminated structures.

The problem with using UV/EB chemistry in laminated structures is the lack of understanding of the interactions that exist within the structure. The interaction between UV/EB ink, whether its flexo or litho, and the substrate is well studied and understood. Also understood is the interaction between the cured UV/EB inks and the various coatings that are used. In a laminate structure different interactions occur and difference forces are introduced that affect the performance of the ink. Within a laminate structure you have several different layers that must work in concert.

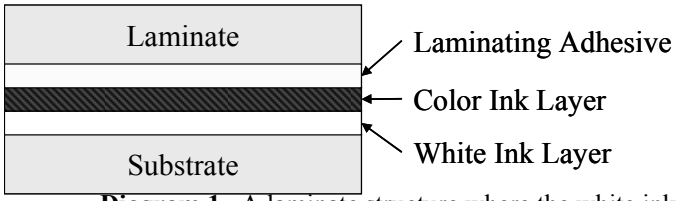

Diagram 1. A laminate structure where the white ink is printed on the substrate.

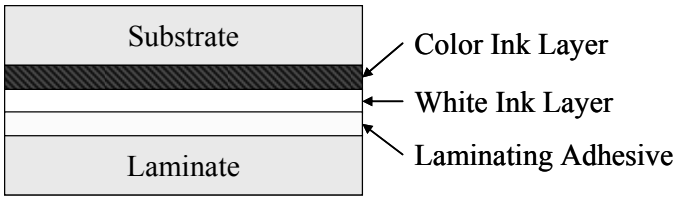

Diagram 2. A laminate structure where the color layer is reverse printed onto the substrate.

For an explanation of laminate structures we will use Diagram 1. Starting at the bottom of Diagram 1 you have the substrate, usually PET, OPP, PE, or a metallized film, that is being printed on. The substrate not only acts as a surface to accept the printing, but also acts as a functional barrier between the ink layers and the packaged good. The functional barrier can be designed to prevent migration of species, especially organic materials, water, oxygen, and nitrogen. In this structure you would then print down a white ink to act as an opaque backing so that the true colors can be seen or to hide what is within the packaging. As an alternative, a white substrate could be used. The white ink needs to have excellent adhesion to the printed substrate below. On top of the white ink the colored, imaged area is printed. An alternative structure is seen in Diagram 2. In this structure the image is reverse printed and then backed with a white ink. Both laminate structures are widely seen. The color ink layer must have good intercoat adhesion to both the white ink layer beneath it and the laminating adhesive that is on top.

A laminating adhesive is applied between the color ink layer and the substrate. Laminating adhesives can be broken down into four different types: water borne, solvent borne, 100% reactive (includes UV/EB, 2-part urethane, and polyester), and hot melt. The choice of adhesive is guided by the desired end properties of the laminate structure and the available application equipment. The adhesive must have excellent adhesion to the color ink layer and also to the laminate (or second substrate) that is put on top.

Experimental

A study was undertaken to understand the interactions that can take place within the structure and how different oligomer types can affect the final performance of the structure. In order to isolate the UV/EB ink components a more simple laminate structure was used. In Diagram 3 you can see that the white ink layer has been removed. This is for two reasons. First, having the white ink in the system adds another layer where failure can occur. It is harder to control and interpret what is happening between the two layers of ink. Second, making a white ink does not allow for the same amount of variance in oligomer type and amount that can be done when using colored ink.

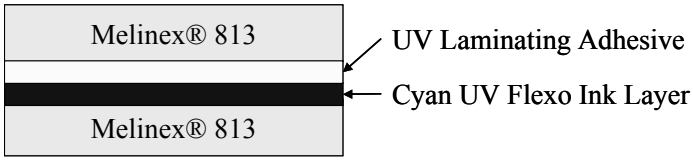

Diagram 3. Laminate structure used in this study.

The substrate and laminate chosen was 2-mil Melinex® 813, available from DuPont Teijin Films. The Melinex® 813 is a polyethylene terephthalate (PET) film that is coated with a water based coating to improve adhesion. Melinex® 813 is commonly used in laminate structures for food packaging. The UV laminating adhesive is one that is commercially available and designed for PET to PET laminations.

All of the inks used in the study were cyan UV flexo inks. UV flexo printing was chosen as an application method because many laminate structures are printed using a flexographic printing process. Also, the ink more readily accepts various kinds of oligomer chemistries and more consistent prints can be obtained using lab-scale flexo printing equipment. All of the ink prints were made using a HarperScientific Phantom™ hand proofer equipped with a 600 line / in. (2.41 bcm) anilox roll. The standard UV flexo formulation in Table 1 was used for all of the cyan inks.

Component	%	Purpose or Structure
Oligomer or monomer	35.0	Component to be evaluated
Ciba® Irgalite® Blue GLVO	20.0	Cyan pigment
CD562	11.0	Acrylate Ester
SR492	10.5	Propoxylated Trimethylolpropane Triacrylate
Polyester Acrylate	10.0	Pigment wetting
Ciba® Irgacure® 369	3.5	2-Benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone
Lamberti Esacure® KS300	3.0	Alpha-hydroxycyclohexyl-phenyl ketone
Lamberti Esacure® TZT	1.0	Blend of Methylbenzophenone and Trimethylbenzophenone
Lamberti Esacure® ITX	0.5	Isopropylthioxanthone
Lubrizol Solsperse® 39000	5.0	Hyperdispersant
Byk®-UV3510	0.5	Silicone wetting aid

Table 1. Cyan UV Flexo formulation used for the evaluations.

Thirty five percent of various types of oligomers or monomers were incorporated into the formulation and evaluated. CD562 (EO HDDA) was used to lower the viscosity and to provide some adhesion onto the Melinex® 813. To increase the cure speed and cross link density SR492 (PO TMPTA) was used. The pigment wetting package consisted of 10% of polyester acrylate and 5% of Solsperse® 39000, a hyperdispersant. The photoinitiator package consisted of a blend of four components designed to cure pigmented ink with a medium pressure Hg arc lamp. Byk®-UV3510 was added to improve substrate wetting, especially when components with high surface tension were used. The Byk®-UV3510 did not affect the lamination strength of the systems tested.

The UV flexo inks were printed onto the PET, then cured at 100 fpm using a Fusion 600 W/in H lamp at 70% power. This gave an integrated energy of 76 mJ/cm^2 on an International Light IL390 radiometer. To test for cure speed of the inks the belt speed of the curing unit was adjusted to decrease the energy delivered to the ink. The UV laminating adhesive was drawn down and nipped at the same time on top of the printed and cured UV flexo ink. The adhesive was cured at 50 fpm using a Fusion 600 W/in D lamp at 100% power for an integrated energy of 625 mJ/cm^2 on an International Light IL390 radiometer.

Fifteen different monomers and oligomers were evaluated for various properties relating to the lamination. The components are listed in Table 2.

	Chemistry	Unique Attribute	Acrylate Functionality
Monomer 1	Diacrylate Monomer	High T_g, hard	2
Monomer 2	Triacrylate Monomer	Cross link density	3
Oligomer 1	Epoxy Acrylate	Flexible	1
Oligomer 2	Epoxy Acrylate	High T_g, hard	2
Oligomer 3	Epoxy Acrylate	High T_g, hard	2
Oligomer 4	Urethane Acrylate	Flexible	2
Oligomer 5	Urethane Acrylate	Hard	2
Oligomer 6	Urethane Acrylate	Very flexible	2
Oligomer 7	Polyester Acrylate	Abrasion resistant	4
Oligomer 8	Polyester Acrylate	Tough	4
Oligomer 9	Polyester Acrylate	Hard	6
Oligomer 10	Acrylated Amine	Surface cure	2
Oligomer 11	Modified Polyether Acrylate	Surface cure	4
Oligomer 12	Polyester Acrylate	Adhesion, flexibility	1
Oligomer 13	Acrylic Oligomer	Adhesion, hard	2

Table 2. List of different monomers and oligomers that were tested.

The components were chosen based on chemistry type and on the different physical properties that they can bring to a formulation. For example, three different urethane acrylate oligomers were evaluated. The first one, Oligomer 4, is a low viscosity oligomer that is flexible and tends to have good adhesion on films. The second one, Oligomer 5, is a lower molecular weight, high T_g oligomer. The third one, Oligomer 6, is a high molecular weight, low crosslink density, low T_g oligomer. By examining the way that oligomers with similar cured properties, but different chemistries behave we can understand the performance of a laminate system.

The inks were first evaluated for their liquid ink properties. Each flexo ink was made as an entire ink, not from a common dispersion, to ensure the best properties could be achieved. The inks were passed over a three roll mill four times to ensure proper dispersion. All of the inks showed no particles on a Hegman grind gage. Once milled, each ink's rheology was measured using a Brookfield DV-III rheometer equipped with a CP42 spindle. Table 3 contains the results of the testing.

	Yield Stress (D/cm)	Plastic Viscosity (cps)	Cure Speed (fpm)
Monomer 1 Ink	0.1	365	675
Monomer 2 Ink	0.8	431	400
Oligomer 1 Ink	0.4	608	500
Oligomer 2 Ink	0.7	5572	800
Oligomer 3 Ink	0.9	6596	650
Oligomer 4 Ink	0.5	1970	350
Oligomer 5 Ink	0.8	2565	500
Oligomer 6 Ink	0.7	6831	300
Oligomer 7 Ink	0.4	477	500
Oligomer 8 Ink	0.8	4174	400
Oligomer 9 Ink	0.7	2183	450
Oligomer 10 Ink	0.5	799	450
Oligomer 11 Ink	0.4	744	800
Oligomer 12 Ink	0.6	5343	350
Oligomer 13 Ink	3.2	7539	150

Table 3. Liquid properties of the cyan UV flexo inks.

As expected, the viscosity of the ink varies greatly with the viscosity of the different monomers and oligomers that are added. The inks based on Oligomers 2, 3, 6, 12, and 13 were very viscous and difficult to achieve consistent prints. That being said, some of the very viscous oligomers used in this study could not be used at high percentages in a commercial UV flexo ink. Evaluation of them is necessary as they could be used at lower levels in a UV flexo ink or in a UV/EB litho ink.

The difference in cure speed among the UV flexo inks is dependant on three factors: the homopolymer T_g, the acrylate functionality, and the abstractable hydrogens of the different monomers or oligomers. Monomer 1 and Oligomers 2, 3, 5, and 7 show fast cure speed because they have high T_g backbones and can increase the T_g of the ink. Hence the ink will develop physical properties (aka scratch resistance) more quickly. Monomer 2 and Oligomers 8 and 9 owe their cure speed to having higher acrylate functionality. Oligomers 1, 10, and 11 have sources of abstractable hydrogen and, when coupled with a Type II photoinitiator, show good cure speed. The slowest curing materials, Oligomers 4, 6, 12, and 13 are lower T_g materials.

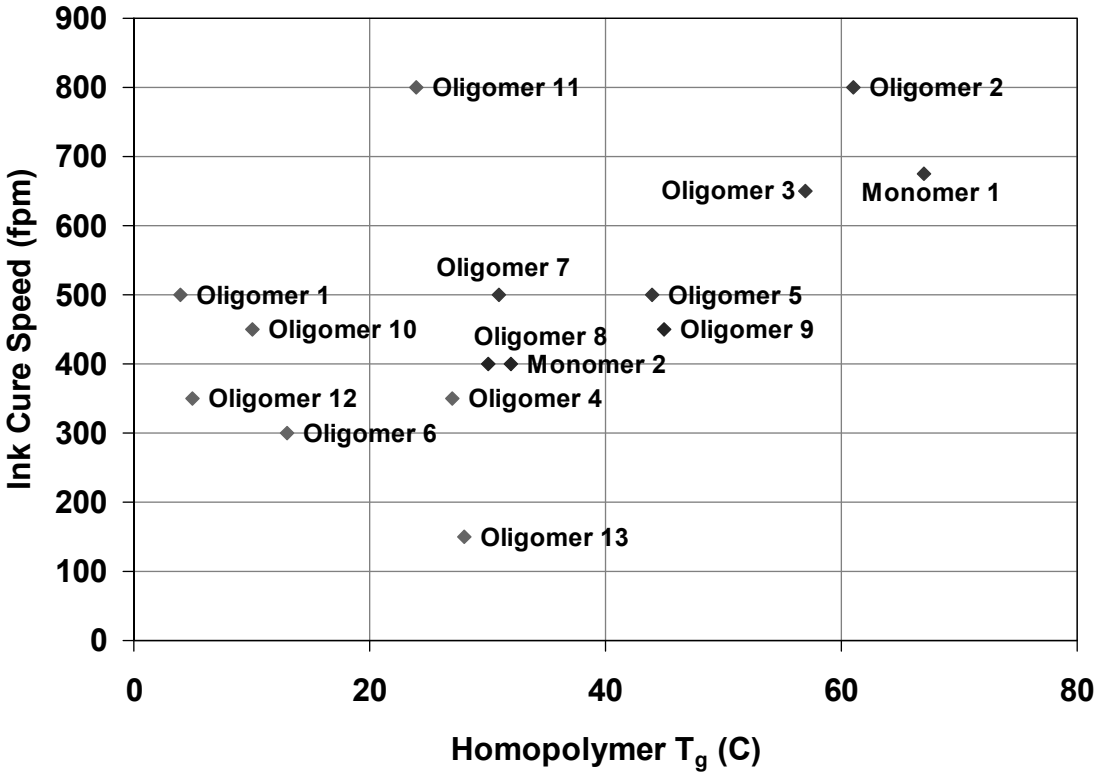

Diagram 3. Homopolymer T_g of the monomer or oligomer compared to the cure speed of the cyan UV flexo ink made with the same monomer or oligomer.

If you graph the homopolymer T_g (by DSC) of the monomers or oligomers used in the ink versus the cure speed you can see some interesting trends. The monomer and oligomers, the red marker series, have high T_g backbones and show faster cure speed than the other backbones. The oligomers, the green marker series, with readily abstractable hydrogen atoms in their backbones show faster cure speed than their lower T_g's would suggest. The higher acrylate functional monomers and oligomers, the purple marker series, do not have high T_g backbones, but the higher functionality raises the T_g of the cured system. The slow curing oligomers, the blue marker series, owe their low cure speed to a combination of low T_g and low acrylate functionality.

Fast cure speed is a nice property to have, however that doesn't mean anything unless adhesion to the desire substrate is very good. Adhesion was tested two different ways. The first was using 610 tape adhesion. Crosshatch adhesion could not be performed because the PET film was very thin. The second was ice crinkle adhesion. The prints were submerged in ice water for 15 minutes then removed and quickly checked for adhesion by scratching the ink. The results are summarized in Table 4.

	610 Tape Adhesion	Ice Crinkle Adhesion
Monomer 1 Ink	100	100
Monomer 2 Ink	100	100
Oligomer 1 Ink	100	100
Oligomer 2 Ink	0	0
Oligomer 3 Ink	90	100
Oligomer 4 Ink	100	100
Oligomer 5 Ink	100	100
Oligomer 6 Ink	0	0
Oligomer 7 Ink	100	100
Oligomer 8 Ink	75	100
Oligomer 9 Ink	100	100
Oligomer 10 Ink	100	100
Oligomer 11 Ink	100	100
Oligomer 12 Ink	100	100
Oligomer 13 Ink	100	100

Table 4. Adhesion test results of the fifteen inks onto PET substrate.

The inks, except for the ones based off of Oligomers 2, 3, 6, and 8 showed excellent 610 tape adhesion to the Melinex® 813. Oligomers 2 and 3 had higher T_g's and were more brittle than the other oligomers tested. Oligomer 3 did pass the ice crinkle test whereas Oligomer 2 failed. This is due to the lower T_g of Oligomer 3 and of the ink. Oligomers 6 and 8 were more flexible oligomers, so brittleness was not an issue when testing their adhesion. Oligomer 8 showed good adhesion, and only had a few areas where adhesion of the ink was lost. In the ice crinkle test Oligomer 8 passed. Oligomer 6 was a high molecular weight urethane acrylate that had a high surface tension and produced a weak cured film. Both were causes to the failure of the adhesion of the ink. If the ink had good, if not perfect, tape adhesion then the ink also had good ice crinkle adhesion as well. As you will see later on, the adhesion of the cyan UV flexo ink is critical to the overall strength of the laminate system.

Crosslink density of the various cured inks was measured using both methyl ethyl ketone (MEK) and isopropyl alcohol (IPA) rubs. A cotton rag that was soaked in either MEK or in IPA was rubbed on the cured ink area and the number of rubs was counted, as shown in Table 5.

	MEK Double Rubs	IPA Double Rubs
Monomer 1 Ink	8	36
Monomer 2 Ink	6	45
Oligomer 1 Ink	1	9
Oligomer 2 Ink	15	90
Oligomer 3 Ink	4	100
Oligomer 4 Ink	3	15
Oligomer 5 Ink	13	150
Oligomer 6 Ink	8	35
Oligomer 7 Ink	3	20
Oligomer 8 Ink	2	25
Oligomer 9 Ink	8	25
Oligomer 10 Ink	2	9
Oligomer 11 Ink	3	35
Oligomer 12 Ink	1	7
Oligomer 13 Ink	2	5

Table 5. Number of double rubs necessary to see a break in the cured UV flexo ink film.

The results from the double rub testing vary widely. The MEK rubs were found to be too aggressive on the thin, pigmented film and gave results that did not show enough difference in the values. IPA double rubs, however, gave a nice range in values that could be analyzed. The lower T_g materials with low crosslinking, like Oligomers 1, 4, 7, 10, 12, and 13, had very low IPA double rub resistance. The higher T_g materials, whether by backbone structure or by crosslinking, showed much better IPA double rub resistance.

The goal of the initial phase of this project was to understand the interactions between the UV flexo ink oligomers and the UV laminating adhesive that was used to assemble the structure. The current commercial UV laminating adhesives, like all UV/EB systems, contain some acrylate monomer in the liquid system. In a UV laminating adhesive the monomers tend to be low T_g, low molecular weight, and adhesion-promoting monomers so as to give the adhesive its desired cured properties. In systems for plastics, the monomers promote adhesion by "biting" into the substrate. Upon cure an interpenetrating network (IPN) is formed that then ties the adhesive to the substrate through covalent bonds. The next part of the project looked at the resistance of all of the different cured inks to different monomers that are commonly found in UV laminating adhesives. Table 6 shows the results of the monomer analysis.

	TMCHA Resistance	EOEOEA Resistance	THFA Resistance	PEA Resistance	TDA Resistance	IBOA Resistance
Monomer 1 Ink	IR	IR	IR	IR	IR	IR
Monomer 2 Ink	NE	NE	NE	NE	NE	NE
Oligomer 1 Ink	NEA	IR	IR	IR	I	I
Oligomer 2 Ink	NEA	I	NEA	I	I	NEA
Oligomer 3 Ink	I	IR	IR	I	I	NEA
Oligomer 4 Ink	NE	NE	NE	NE	NE	NE
Oligomer 5 Ink	I	I	I	I	I	I
Oligomer 6 Ink	NE	NEA	IR	IR	NE	NEA
Oligomer 7 Ink	NEA	I	I	I	NE	NEA
Oligomer 8 Ink	NE	I	I	I	NE	NE
Oligomer 9 Ink	NE	NE	NE	NE	NEA	NEA
Oligomer 10 Ink	NEA	NEA	NEA	NE	NEA	NE
Oligomer 11 Ink	NE	NE	NE	NE	NE	NE
Oligomer 12 Ink	IR	IR	IR	IR	NE	IR
Oligomer 13 Ink	I	I	I	I	I	I

Table 6. Effect of the six different monomers on the cured UV flexo inks. NE = No Effect; NEA = No Effect Ink Absorbed; I = Intermediate Effect; IR = Ink Removal

A drop of each monomer was placed onto the printed and cured area of the different cyan UV flexo inks. The drop of monomer was allowed to sit on the sample for 15 minutes while at room temperature (nominally 23˚ C). After 15 minutes the drop was wiped off and the result was noted. For the effects the following notations were used: NE = No Effect; NEA = No Effect Ink Absorbed; I = Intermediate Effect; IR = Ink Removal. "NE" explains itself. In the "NEA" samples the ink, and possibly the substrate, absorbed the monomer that was placed on it. "I" denotes some intermediate effect where the monomer did something to the ink, but did not remove it. "IR" means that the ink was wiped off where the monomer drop was.

Interesting trends could be found within this data set. As expected, Oligomers 1, 6, 12, and 13 had low crosslinking and were susceptible to attack from the aggressive monomers. The ink was either removed or showed dramatic effects from the monomers. Monomer 1 and Oligomers 2, 3, 5, and 6 had good resistance to the IPA double rubs but were able to be effected by the test monomers. Interestingly enough, all five of these materials had two acrylate groups per molecule, hence low crosslinking and the monomers could penetrate the cured ink film. Monomer 2 and Oligomers 7, 8, and 9 had acrylate functionality higher than two acrylates per molecule and performed well. Apparently the additional crosslinking from the higher functionality increased the monomer resistance. Also interesting was the effect of amine compounds on monomer resistance. Despite being lower acrylate functional, Oligomer 10 showed good resistance to the monomers. The higher acrylate functional and amine functional Oligomer 11 showed excellent resistance to the monomers. Both of these materials owe their excellent monomer resistance to additional curing of the surface due to Norrish Type-II photoinitiator reactions.

Finally, to pull together all of the other testing the inks were incorporated into a laminate structure. Remember, the cyan UV flexo inks were printed onto Melinex® 813. After the inks were cured, then the laminating adhesive was applied and nipped between the printed Melinex® 813 layer and an unprinted sheet of Melinex® 813. To cure the UV laminating adhesive the entire structure was cured using a Fusion 600 W/in D lamp at 100% power for an integrated energy of 625 mJ/cm^2 on an International Light IL390 radiometer. The cured samples were cut into 1 inch strips then tested for their peel strength on an Instron Tensile Tester. The adhesive thickness was 10 – 13 µm. A thicker adhesive film was chosen to achieve higher T-Peel Strengths that could show differences between the inks.

	T-Peel Strength (lb.-F)	Failure Mode
Monomer 1 Ink	0.28	AFI
Monomer 2 Ink	1.48	C
Oligomer 1 Ink	0.17	AFI
Oligomer 2 Ink	0.04	AFI
Oligomer 3 Ink	0.05	AFI
Oligomer 4 Ink	0.24	C
Oligomer 5 Ink	1.08	C
Oligomer 6 Ink	0.10	AFI
Oligomer 7 Ink	0.25	C
Oligomer 8 Ink	0.05	AFI
Oligomer 9 Ink	0.13	AFI
Oligomer 10 Ink	0.63	C
Oligomer 11 Ink	0.17	C
Oligomer 12 Ink	0.22	AFI
Oligomer 13 Ink	0.32	AFI

Table 7. Peel strength and failure mode results of the T-Peel testing of the laminate structures.

The value reported in Table 7 is the average of five different samples that had the same failure mode. For each sample within a specific ink the strength is an average of the force during the entire T-Peel test. The laminate structures that were tested only showed two different failure modes, Cohesive (C) and AFI (Adhesive Failure Ink). In the Cohesive failure the failure was between the ink and the adhesive layer. In the AFI failure the ink lost adhesion to the Melinex® 813 that the ink was printed on. The Melinex® 813 - laminating adhesive - Melinex® 813 structure had a T-Peel strength of 1.16 lb.-F.

To start with, the inks that did not have excellent adhesion to the Melinex® 813 (see Table 4) had the lowest T-Peel strengths and also all showed AFI failure. Oligomers 2, 3, 6, and 8 were in this group. So in order for you to have a strong lamination with the ink layer, you must first have excellent adhesion to the substrate that is printed on. To save time, the adhesion of the ink onto the substrate can be used as a screening tool to eliminate systems that will not have a good lamination.

Another group of inks exhibited higher T-Peel strengths, although their strength was still too low to be considered for a commercial system. Monomer 1 and Oligomers 1, 9, 12, and 13 had higher T-Peel strengths than the previous group, but still had AFI failures. Monomer 1, and Oligomers 1, 12, and 13 showed susceptibility to different aggressive monomers that were applied on top of the cured ink. If

the inks in the adhesive were able to penetrate the ink film they could act as plasticizers or solvents that affected the adhesion of the ink film on the PET. Oligomer 9 was not pervious to the monomers, but may have had borderline adhesion to the PET layer.

The final group of inks all showed Cohesive failure with different T-Peel strengths. Oligomers 4, 7, 10, and 11 all had T-Peels of less than 1 lb.-F. The inks made from these materials all had excellent adhesion to the PET substrate. Also, all five of the materials showed good to excellent resistance to the aggressive monomers, therefore the ink film was not as affected by the laminating adhesive put on top. Only two of the inks, based on Monomer 2 and Oligomer 5, had T-Peel strengths of greater than 1 lb.-F. What sets these two inks apart from the others? They both had similar resistance to the aggressive monomers. The best corollary can be drawn between the homopolymer T_g of Monomer 2 and Oligomer 5. Both of their T_g's were from 30 – 50 ˚C. Perhaps if the T_g is lower than this the ink film is too soft and will not give good T-Peel strength. If the T_g is higher than this range then maybe the ink film becomes too brittle.

Conclusion

By changing the monomer or oligomer chemistry incorporated into a UV flexo ink the lamination properties can be dramatically affected. The adhesion of the ink to the printed substrate, the T_g of the monomer or oligomers used, and the resistance of the cured ink to aggressive monomers in the UV laminating adhesive are all key parameters in the strength of the laminate structure.

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