Developing Formable Properties in Energy Curable Flexographic Inks

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Abstract

This paper investigates technical approaches to address a growing interest in the printing market for energy curable flexographic inks that can be formed post cure. Factors such as backbone chemistry, crosslink density, molecular weight, and ink properties are evaluated to select optimum chemistry. Testing focuses on a white ink formulation and correlations are drawn between physical properties and heat shrink application tests.

Labeling industry

Consumer product companies increasingly are looking at new ways to use labels to differentiate their products from competitive ones, in an effort to attract customers. The labeling industry historically has relied on paper labels adhered to packages but this technology has limitations, principally that the labels tend to hide or obscure the product inside the package. The trend is towards the "close to bottle" or label-less look of shrink sleeve labels.

A comparison of the paper label and shrink sleeve technologies can be seen in Figure 1. The use of shrink film for labeling allows for an increased surface area to enhance brand recognition on the package. Shrink technology also allows for a 360 degree labeling of a container. By relying on the pressure from the shrink process to adhere the label, shrink sleeve packaging eliminates the adhesive required for paper labeling and therefore presents a sustainability advantage.

Figure 1 - shrink vs. paper label

Shrink Sleeve Process

Shrink sleeve label production is compatible with a wide variety of printing technologies, including flexography, gravure, digital, rotary, and offset. The selected printing technology depends on the printer, print run length, and the end properties desired. Typically, flexography and gravure printing are used for longer print runs while digital technology is used for shorter runs. While the focus in this study is on UV-based materials, waterborne and solvent-based inks also have a significant presence in this market.

Flexographic, or flexo, shrink sleeve labels tend to be reverse-printed, which means the ink is on the inside of the label. This protects the finished print from scratching and marring, and insures a high gloss surface appearance after shrinking. After the shrink film is printed and seamed to form a sleeve, it is placed over the container, exposed to heat, and shrink-wrapped to the exterior shape of the container. Typical methods to shrink the film in automated processes are dry heat, steam, a combination of the two, or in some cases, immersion in hot water. The dry heat method can be done by infrared (IR) heating or with hot air convection systems. The temperature and duration of the shrink process is dependent on the polymer film used as the shrink substrate.

When choosing a substrate to use for printing tone must consider the degree of shrink required based on the size and shape of the container. The most commonly used substrates for shrink sleeve applications are polyvinyl chloride (PVC), oriented polypropylene (OPP), and polyethylene terephthalate glycol (PETG). The properties of PVC, such as low cost and a high degree of shrink-ability, make it a popular choice for shrink sleeve labels. Oriented polypropylene is also a low cost substrate, but is limited in shrink-ability.

For shrink sleeve applications that use UV-cured inks PETG is the most commonly used substrate. PETG offers a very high degree of shrink potential, enabling a wide range of design freedom. All the work reported in this study was done using PETG film, Transept™ 8A from the Transilwrap Company. The properties of this shrink film are shown in Table 1.

PROPERTIES	UNIT OF MEASURE	Gauge	TEST METHOD
Thickness	Microns	50	Transilwrap Test
Coefficient of Friction	Kinetic	0.24	ASTM D882A
Tensile Strength MD	psi	8043	ASTM D882A
Tensile Strength TD	psi	27,950	ASTM D882A
Elongation at Break MD	%	565	ASTM D882A
Elongation at Break TD	%	52	ASTM D882A
Haze	%	2.8	ASTM D1003
Elmendorf tear Strength MD	g/ply	250	ASTM D1922
Elmendorf tear strength TD	g/ply	19	ASTM D1922
Shrinkage stress	MPa	6.3	BAC Method
Specific Gravity	NA	1.31	BAC Method
Ring Crush	N	8.1	TAPPIT 818

Table 1-Transept ™ 8A properties

Experimental Study

The intent of this experimental study was to develop an understanding of how different formulation factors, including backbone structure, functionality, and molecular weight, as well as the cured ink physical properties, influence the shrink performance of UV-curable inks. The ultimate goal was to provide guidance for successfully formulating a UV-curable flexographic ink for shrink sleeve applications. The experimental approach was focused on understanding the performance of a flexo white base ink. Due to the higher print thickness of a white base ink compared to process colors, it possesses the greatest performance challenge. Using a 200 anliox hand proofer from Harper Scientific, we applied 5.2 – 7.6 BCM (billion cubic microns) to PETG films for testing.

A shrink mold shown in Figure 2 was designed to shrink films over a range 0% to 85%. The degree of shrink was changed by adjusting the diameter of the PVC pipe seen in the center of the shrink mold between the two disk-shaped end caps. By decreasing the diameter of the PVC pipe we could increase the degree of shrink, and vice versa. The degree of shrink may be quantified by the circumferential reduction between the starting shrink sleeve and the final part, as shown in Equation 1.

$$Shrink = \frac{Initial\,Area - Final\,Area}{Initial\,Area} = \frac{2\pi r_0 L - 2\pi r_1 L}{2\pi r_0 L} = \frac{r_0 - r_1}{r_0}$$

Equation 1 - Shrink calculation

The experimental method and % shrink calculation were validated by shrinking a 1cm square-patterned film and measuring the change in dimensions of the pattern. A 50% shrink mold would be predicted to reduce the lateral 1 cm squares to ½ cm squares, which was verified experimentally.

Films were seamed using cyanoacrylate glue after printing. Each test sleeve was seamed with a diameter slightly larger than the mold to allow it to slip easily over the mold prior to shrinking. Shrinking was done in a test chamber at a temperature of 90°C and relative humidity of 90% for 1 minute. After shrinking was complete, the film was cut away from the mold for evaluation and testing. Unless otherwise noted shrink testing was performed using a 50% shrink mold.

Figure 2– Shrink Mold and Performance Criteria

Shrink performance was evaluated using a visual rating scale (0 to 4, 0=worst, 4=best), where cracking and loss of adhesion were used as the basis for the rating. Adhesion testing was done using crosshatch adhesion testing with Scotch® brand 610 tape. In addition to crosshatch testing, an ice water crinkle test was used to assess adhesion. In this test cured ink samples were submerged in an ice water bath for 30 minutes. The samples were then removed from the water and deformed (crinkled) for 15 seconds, then visually evaluated for adhesion loss on a scale of -1 to 1 (refer to Figure 3).

Figure 3- Crinkle Performance Scale

Another important performance test was a blocking assessment. The issue of blocking occurs when there is unwanted adhesion between two surfaces (for example, between surfaces in contact on a roll of film). To test for blocking, we put cured samples under pressure and heat (30 inch-pounds of torque on the bolts for 24 hours at 60°C) to simulate conditions on a roll (blocking test fixture shown in Figure 4). The final and very important ink performance property is its cure response. We used both the "thumb twist" and "nail scratch" methods. Both are quick and effective pass/fail tests commonly used in the ink industry to evaluate cure. Table 2 summarizes the tests used to evaluate properties of the shrink sleeve inks.

Figure 4- Blocking Test Fixture

Test	Scale	Description
Shrink	**0 to 4**	**Visual inspection, cracking, adhesion loss post shrink**
Blocking	**-1 to 1**	**Visual inspection looking for ink transfer**
Finger nail scratch	**Pass/Fail**	**Does it scratch off or not**
Ice water crinkle	**-1 to 1**	**Looking for loss of adhesion**
Cure Speed	**Pass/Fail**	**Thumb twist**

Table 2- Properties tested

Backbone/Functionality Relationship

Different chemical backbones with varying acrylate functionality were studied to determine the effect they would have on the printing, curing, and shrink properties of the UV-cured ink formulations. Backbone materials tested included polyester acrylates, urethane acrylates (aromatic and aliphatic), epoxy acrylates, and acrylated acrylics. Physical properties of UV-curable resins are affected by both molecular weight and degree of functionality, which can be represented by a combined quantity, equivalent

weight. The equivalent weight (see Equation 2) gives an assessment of the idealized molecular weight between crosslinks and, in general, correlates with physical properties.

$$Equivalent\ weight = \frac{Molecular\ Weight}{Acrylate\ functionality}$$

Equation 2 - Equivalent weight calculation

Inks were cured using a single 300 w/in Hg arc lamp at a line speed of 100 ft/min. The UV dose under these conditions was 150 mJ/cm^2 measured with an EIT Power Puck II. While typical flexo press line speeds range from 100-600 ft/min, our study was conducted at the lower end to assure full cure of the test specimens.

To evaluate the effect of various monomers ranging in equivalent weight on shrink performance a standardized ink formulation was developed using a single monofunctional epoxy acrylate oligomer. Figure 5 demonstrates the impact that the low molecular weight monomers studied have on cure response and shrink performance. The results show that low equivalent weight monomers lead to better cure speeds; however the shrink performance was relatively poor for all the samples and did not change much with the particular monomer used. Application properties such as blocking, nail scratch, and crinkle resistance correlated with the degree of cure. The effect of varying monomer equivalent weight on key application properties is shown in Table 3. Optimization of these properties was a secondary objective because identifying the formulating space for good shrink performance is the primary objective of this work.

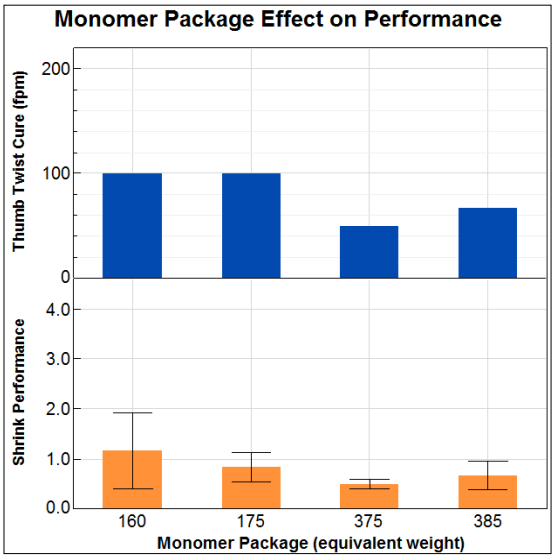

Figure 5- monomer based performance

37.4% Oligomer 6.0% Disp Oligomer 6.6% Variable 40% TiO_2 2.0% Dispersant 8.0% PI	Eq. wt. of monomer	Adhesion	Blocking	Crinkle
	164	1	0	-1
	208	1	0	-1
	210	1	-1	-1
	344	1	-1	0
	448	1	-1	-1

Table 3- application property results

A follow-up study, based on the formulation used in the monomer equivalent weight experiments, was done to evaluate a range of typical acrylate oligomers with varying backbone structures. The monomer used in the formulation was kept constant. Figure 6 shows the shrink performance as a function of backbone chemical structure and equivalent weight. In general, as can be seen in this figure, each backbone structure family has some formulations that have good shrink performance and others with mediocre or poor shrink performance. The results indicate no preference for the

chemical species present in the backbone, whether they were ethoxylated, propoxylated, or alkane structures. While successful formulations have been developed for shrink performance within this experimental design, no clear trend could be determined based on the backbone chemical structure. The benefit of this outcome is that the backbone structure may be chosen to optimize other (non-shrink) properties.

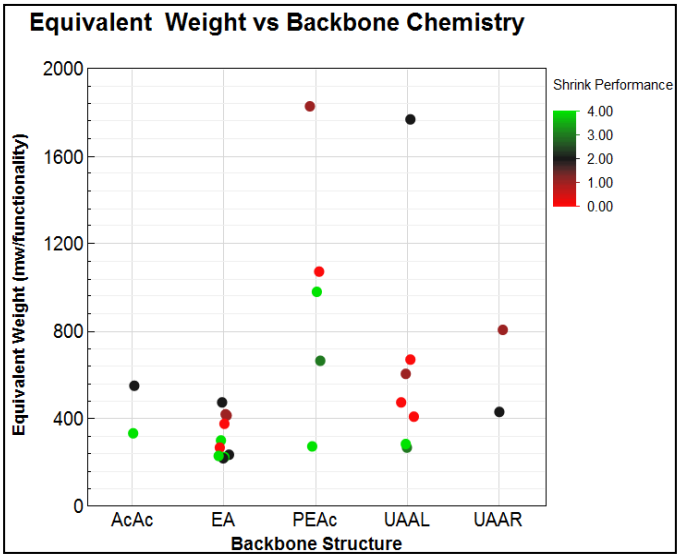

Figure 6 - Backbone Performance

Physical property influence

Physical properties of polymers play a pivotal role in their success or failure in a given application. In order to get a better understanding of the underlying basis for the shrink results seen in the backbone structure study, we measured the physical properties of oligomers for correlation with shrink performance. Cured, neat oligomers were evaluated using standard physical property test methods. Each sample was prepared using a standardized photoinitiator package at a 6% level and was coated at a 5 mil film thickness on an aluminum mill panel from Q-Panel. UV-curing was done with (2) 400 w/in Hg arc lamps at a line speed of 50ft/min. The dose for these samples was 1.8 J/cm^2, as measured by an EIT Power Puck II. Cured samples were left to sit for 24 hours prior to physical property testing.

Dynamic Mechanical Analysis (DMA) was used to determine the T_g of the polymer. The T_g of a polymer depends on the backbone structure, molecular weight, and functionality. Polymers with high T_g will have hardcoat properties such as scratch resistance, chemical resistance, etc. whereas lower T_g polymers will have more adhesive-like properties such as elongation, flexibility, tackiness etc. Instron tensile testing (ASTM D882) was done to gather the TEME (Tensile Stress, % Elongation, 1% Modulus, and Energy) properties of the cured films. The Young's (elastic) modulus is a measure of the stiffness of the material at low strains. A higher modulus indicates that more force is required to deform the material. Tensile strength is the maximum stress recorded during a load and is reported in pounds per square inch (psi). Tensile strain or percent elongation is a measurement of the degree to which the polymer can be

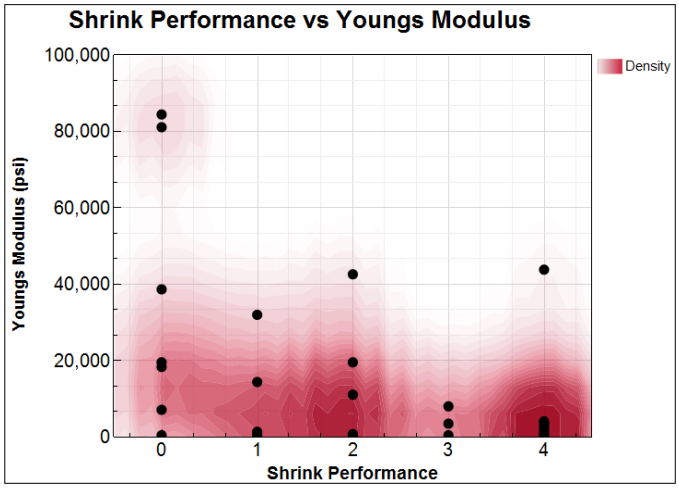

Figure 7 - Shrink Performance vs. Modulus

stretched until it reaches the rupture point. The energy to break is the area under the stress-strain curve, which is commonly referred to as the "toughness" of a material.

No correlation was found between shrink performance and the cured oligomer's % elongation, tensile strength, energy, or T_g. However, the Young's modulus of the inks did correlate with the shrink performance as depicted in Figure 7. We found that, in general, excellent shrink performance requires the formulation to have a low modulus. However, low modulus isn't sufficient, as a low equivalent weight is also critical for providing inks with the highest level of shrink-ability.

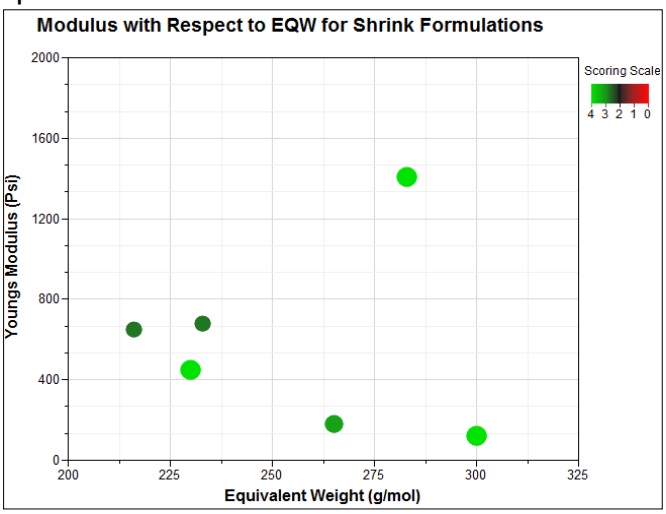

Figure 8- Targeted Modulus and Equivalent Weight Range

The results of a follow-up study are shown in Figure 8. Resins tested in Figure 8 were chosen across a range of backbone chemistries, diluent type, equivalent weight, and monomer concentration. This study demonstrates that keeping the tensile properties (in particular, Young's modulus) and equivalent weight in an optimal range gives inks that will be suitable for shrink applications. This is evident as nearly all of the formulations tested proved acceptable in their shrink performance. There is a huge benefit to this result in that ink chemistry, since it is not necessarily constrained by shrink performance, can be tailored to provide key performance properties in other critical areas such as durability, regulatory compliance, adhesion to particular substrates, or environmental resistance.

Summary

When developing a flexographic ink for shrink sleeve applications several critical factors need to be considered. Through the testing outlined in this paper, we have demonstrated the importance of the intrinsic mechanical properties of the UV-cured ink on shrink performance. Specifically, selection of an ink formulation with a low Young's modulus is of utmost importance in designing an ink with excellent shrink characteristics. This is because the ink must be able to resist a rapid reduction in surface area without buckling and cracking during the shrinking process. Having a low modulus permits the ink to bend and compress as required to produce an un-ruptured print layer on the PETG film substrate. Keeping this concept in mind allows formulators to select materials from a broad range of monomer and oligomer combinations so that other performance requirements (beyond shrink) can be met. The potential to use a wide variety of raw materials opens up the possibility of satisfying other performance objectives such as regulatory compliance, cost constraints, etc. Ultimately, this gives the UV-cured ink technology for shrink sleeves the latitude needed for growth and expansion into new end-use applications.