Recent Advances in Low Viscosity, Low Migration, Fast Curing UV/EB Resin Technology

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Background

There are several critical issues driving technological developments in UV/EB resin technology today, particularly for the fast growing area of food packaging[1]. One is the need for higher cure speeds to meet the requirements for higher flexographic press speeds and corresponding improved efficiency and economics. This is often addressed by the use of high functionality resins. The second factor relates to migration. The combination of high functionality with high molecular weight reduces the probability of unreacted functionalities, and also the probability for any unreacted molecules to migrate. The combination of high functionality and high reactivity can present challenges for adhesion to film[2].

The relationship between cure energy, viscosity, and molecular weight for a wide range of UV monomers and oligomers are shown in Figure 1.[3]

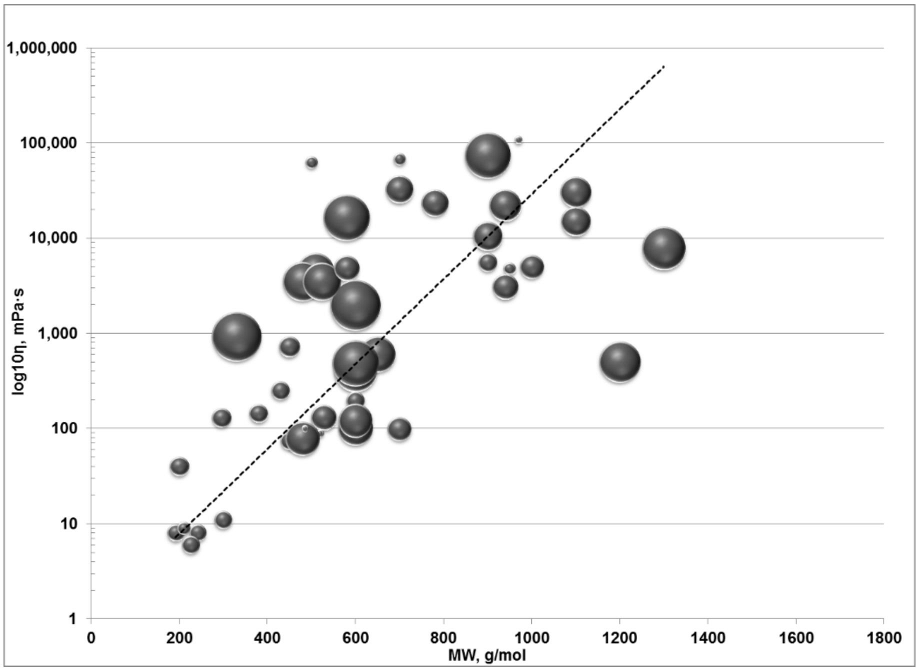

Figure 1. Viscosity vs Molecular Weight of UV Acrylates. (circle size is proportional to cure energy)

Epoxy acrylates, ethoxylates, propoxylates, urethanes, polyesters, and amine modified acrylates are included. Although there are also monomer diluents present in some of the resin systems as well, there is a clear trend of increasing viscosity and cure speed with increasing molecular weight. It is also apparent that the lowest viscosity and lowest molecular weight resins have some of the slowest cure speeds. Other systems which are blends of inert resins with monomers have the expected high molecular weight and high viscosity combined with low curing speed.

The viscosity/MW trend is consistent with the Mark-Houwink equation which describes the relationship between the intrinsic viscosity η and the viscosity averaged molecular weight M_v.[4]

$$[\eta] = K\bar{M}_v^{\alpha}$$

K and *α* depend on the specific polymer and conditions and therefore the slope of log η vs log M_v will depend on the details of the resin chemistry, but there is a general proportionality. For linear polymers, *α* is typically 0.5 - 0.8. The viscosities are usually measured in solvent, and the specific solute-solvent interactions can influence the value of *α* . The η values in Figure 1 were all measured neat. There is a noted exception to the typical *α* values which results from a non-linear or hyperbranched structure.[5]

The application of chemistries with hyperbranched structures in UV/EB applications has been investigated for some time.[6,7,8] The challenge for low migration packaging applications is that high levels of polyol diluents are necessary in order to achieve fluidity at ambient temperature, and the neat hyperbranched polyol is a solid at room temperature[9]. This is presumably due to the polarity of the polyester backbone which comprises the hyperbranched polyol as well as the presence of hydrogen bonding.

Experimental

Low viscosity monomers are often necessary to achieve the rheological properties necessary for flexographic applications, but bring with them challenges relating to migration often due to low molecular weight or low functionality. The higher reactivity resins often bring challenges relating to viscosity, as illustrated in Figure 1. The objective is to achieve a balance between reactivity and diluency.

In order to better understand this effect, a study was made of the viscosity and cure energy of a number of resin compositions. One oligomeric system was selected from the broad categories of epoxy, polyester, urethane, and polyether acrylates. Each oligomer was then blended with DPHA, TMPTA, TPGDA, and HRLV (a novel high reactivity, low viscosity resin). The results of this study are shown in Figure 2.

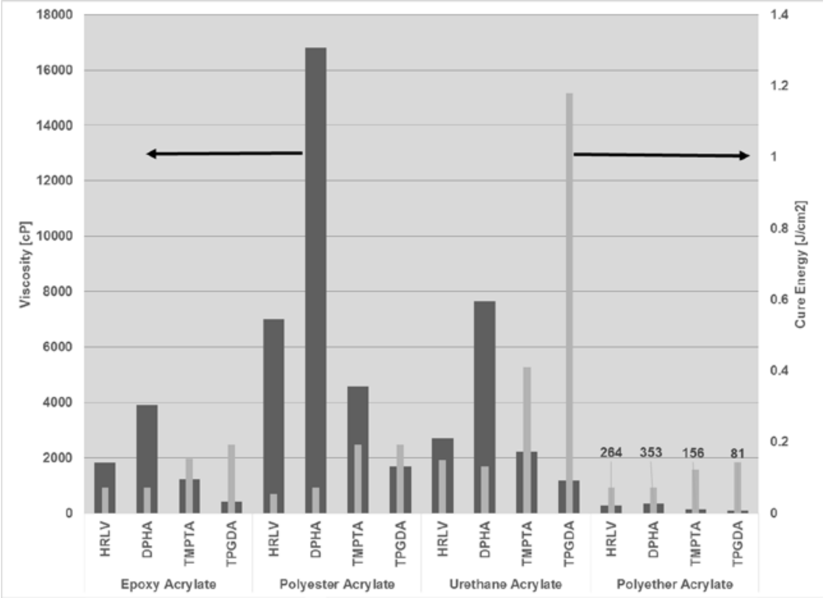

Figure 2. Diluency and reactivity effects in common oligomer systems (black bars represent viscosity, grey bars represent cure energy)[10]

In all cases, the order of viscosity was determined to be TPGDA < TMPTA < HRLV < DPHA. The order of reactivity (higher cure energy) was measured as HRLV ≥ DPHA > TMPTA > TPGDA.

In Figure 1, the data point corresponding to HRLV has a molecular weight of 1200 amu and a viscosity of 500 mPas. Based on the earlier analysis of the Mark-Houwink equation, this resin would be expected to assume a more spherical configuration, which may also be a factor in the higher cure speed of blends which contain HRLV. Despite the differences in polarity and intermolecular interactions within the classes of oligomeric resins in Figure 2, the variation in viscosity and cure speed by addition of the diluent resins follows a consistent trend.

Dispersing additives with spherical structures have been shown to be effective in pigment stabilization in reactive systems[11]. If the HRLV resin assumes a spherical configuration, then it may also have properties in pigmented systems which are different from conventional linear polymers. In order to evaluate this idea, flexo inks were prepared from cyan, magenta, yellow, and black pigments, and tested for cure, color density, and adhesion. The test formulations are shown in Table 1, and the results of this study are shown in Figures 3 and 4.

Dispersion			**Dispersion Letdown**	
Component	**%**		**Component**	**%**
Resin	60-80		Dispersion	50
HMWD[12]	2-4		Epoxy Acrylate	15-25
Pigment	20-40		EOTMPTA	15-25
			PI Blend	10

Table 1. Formulations used in evaluation of flexo ink properties.

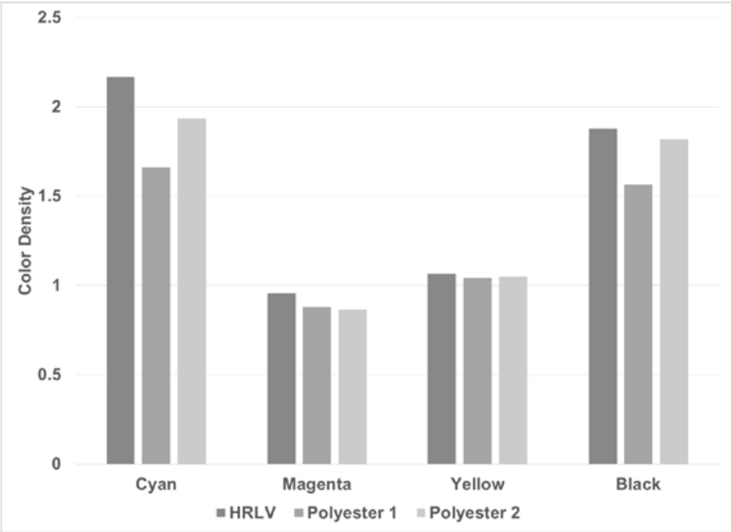

Figure 3. Color density of ink formulations[13]

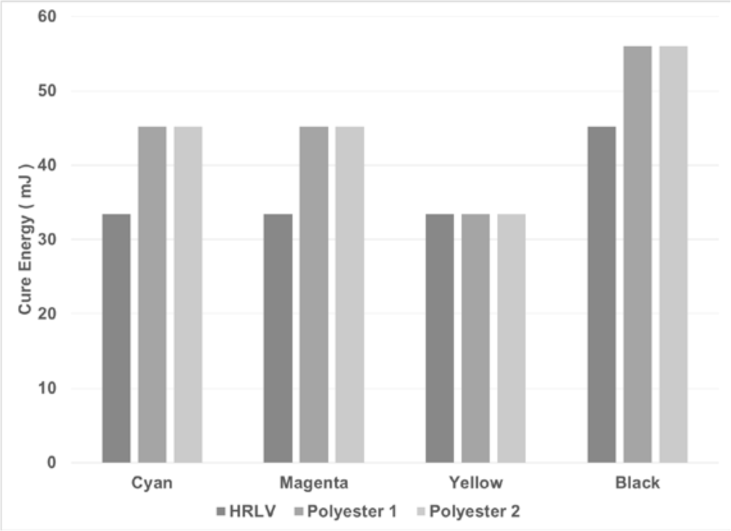

Figure 4. Cure energy of ink formulations[14]

Although there are variations across pigments, there are some clear trends. The two polyester oligomers yield inks with similar color densities and cure speeds. The HRLV resin, presumably with a more spherical rather than linear structure, provides color densities and cure speeds that are superior to the linear polyesters, with the exception of the yellow ink, where the performance is the same. All formulations utilized the same HMWD, and it may be that that the 3 component system of oligomer, pigment, and HMWD could be further optimized in combination with specific pigment chemistries. What is clear, however, is that through the controlled use of the 3 dimensional resin structure, differentiation in ink cure speed and color density can be obtained.

An area for consideration is the possible effect of a non-linear resin on the shrinkage that typically accompanies the UV curing process, and its concomitant loss of adhesion on film. Although there are a number of variables including surface energy that affect adhesion, shrinkage is a very significant factor. The adhesion properties of the ink systems are shown in Figure 5.

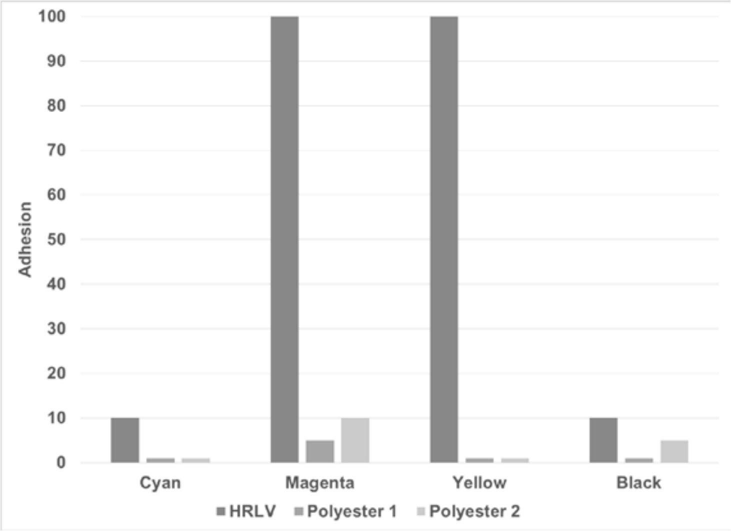

Figure 5. Adhesion properties of ink formulations on untreated OPP

There are clear differences in the adhesion properties between ink systems shown in Figure 5 which do not parallel the trends in the cure energies shown in Figure 4. A slower curing system might be expected to have higher adhesion due to reduced film stress. These results show that the spherical structure of the HRLV not only increases cure speed but increases OPP film adhesion compared to linear polyester oligomers.

Conclusions

The viscosity and molecular weight relationship of commercial UV resins has been examined through the lens of the Mark-Houwink equation in order to understand the effect of molecular shape on performance properties. A resin which was predicted to have a non-linear configuration was also found to provide fast curing speed, high color density, and low shrinkage in flexo ink applications.

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[8] James, D.; Bernquist, H.; Appleqvist, P.; Sandell, P.; Sörenson, K., Radtech 2006 Technical Proceedings

[9] Boltorn™ Product Literature Perstorp Holding AB

[10] Formulations contain a blend of 30% diluent with 66% oligomer and 4% Irgacure™ 500. Numerical values over the polyester data represent viscosity and are added for clarity

[11] Rudolfi, A.; Krohnen, M.; Piestert, F.; Möβmer, S., European Coatings Journal, **11**, 2013, p. 22.

[12] HMWD (High molecular weight dispersant)

[13] Inks applied to OPP at 1.8µ film thickness and formulated to 1000 mPas viscosity. Pigment levels of Cyan, Magenta, Yellow, and Black inks are 15.0%, 12.3%, 10%, and 12.5%, respectively.

[14] Samples cured with D bulb at 1.8µ film thickness.