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Alternatives to energy-cure oligomers based on Bisphenol A (BPA) for printing and packaging applications

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Abstract

Energy-cure oligomers containing Bisphenol A (BPA) impart high chemical resistance, high reactivity and good surface hardness to inks and overprint varnishes used in printing and packaging applications. However, alternatives to BPA-based oligomers are desired due to potential adverse impact on consumer health and safety. In this paper, we will compare BPA-free and BPA-containing acrylates in flexographic applications and discuss performance differences between available options.

1. Introduction

Bisphenol-A (BPA) based acrylates are well known and used in formulating energy-curable overprint varnishes and inks. These materials are derived from Bisphenol-A epoxies with BPA being a precursor. For over 50 years, BPA has been used as an intermediate in the production of epoxy acrylate for applications in energy-curable resins. BPA-containing resins are in widespread use due to properties that they impart to an ink or a coating, such as: high reactivity, outstanding chemical resistances and hardness[1-3]. However, recent developments have triggered a discussion in the ink industry about the safety of BPA-based materials in coatings and inks[4-8]. This is largely due to BPA being suspected to be an endocrine disruptor interfering with the human hormone system and is therefore subject to evaluation by the REACH authorities[14]. Furthermore, in the US, the state of California is taking the lead in regulating BPA-based products, not only plastic articles but also labels and the inks which are printed directly over them. Even if manufacturers of epoxy acrylate based materials do not use pure BPA as a starting ingredient in its UV resin, there is a possibility of it being present in raw materials that could have direct ramification for UV-curable ink formulations and end users. Also, the end users require ink formulations that comply with broad international regulations.

Although raw material selection is key in deciding the regulatory aspects in formulation, formulators also need to make sure that the coatings and inks meet properties that are critical for a printing process, such as print speed, surface cure and through cure, adhesion to a variety of plastic substrates, chemical resistance, color density, gloss, viscosity, scratch resistance, substrate wet out, and hardness, at appropriate coating thickness. These are all critical performance parameters that must be met in formulating an ink or a coating.

This paper and the subsequent presentation is therefore targeted towards formulating overprint varnishes (OPV) and inks with materials that are BPA-free and have properties in line with epoxy acrylate based raw materials.

2. Materials

For packaging, BPA-free inks with performance matching traditional BPA-containing epoxy acrylate based inks are desirable. With this is mind, several candidates such as specialty and polyester resins were investigated in coatings and flexographic ink applications. A BPA-free polyester resin B-1 was selected as a possible candidate in overprint varnishes (OPV) and inks. Initially, we examined the neat properties (**Table 1**) of both BPA-free (B-1) and BPA-based oligomer (EA-1), on curing via electron beam (EB) instead of ultraviolet (UV) curing to ensure 100% oligomeric compositional nature of the films. Cured films of each were prepared by drawing down the oligomer with a #6 rod (~ 60 μm) and curing with EB over a release coated sheet at a speed of 6 m/min, giving a dose of 30 kGy. The oxygen content was maintained below 200 ppm. Both B-1 and EA-1 were cured at 120 keV from the top and peeled and were again subjected to a second exposure from the bottom at 90 keV, to ensure complete cure. Tensile properties were measured via TA Q800 DMA at 25°C and at a strain rate of 10%/min. Elongation and tensile strength were both measured at the point where the sample broke. Glass transition temperature (Tg) was determined on Q2000 DSC with 5 - 9 mg sample in a TZero aluminum pan, subjected to a temperature range from - 90 to 150°C and back down and up at 15°C/min. The Tg's were measured on the second heat at inflection.

Material	Viscosity, cps	Functionality	Elongation at Break	Tg °C	Tensile Strength, MPa
B-1	5000 - 9000	> 3.0	20	2.5	10.6
EA-1	3000 - 6000	> 2.0	1.6	20.1	20.0

Table 1. Oligomers for overprint varnish study and properties

For many instances in both OPV and ink formulations, the use of amino acrylates to circumvent surface cure issues is quite well known. It is known that molecular oxygen impedes complete cure at the surface leading to tacky surfaces, which leads to known issues of blocking during spooling and unwinding process of a printed article[9]. In the presence of oxygen, the active radical reacts readily with the molecular oxygen thereby forming a peroxy radical, rendering tacky surfaces. Amino acrylates are known in this respect to flood the surface with active radicals scavenging the oxygen from the air, forming peroxy radicals which under normal conditions would have prohibited chain growth, making it detrimental in achieving tack-free surface[10]. These amino acrylates also have active hydrogen that forms a new radical initiating a new chain, thus rendering optimum cure at the surface, **Figure 1**[11]. In this regard, several amino acrylates with wide ranging viscosities and functionalities, are useful in formulation design.

The amino acrylate chosen for the OPV formulation used in this study is designated AA-3; and it has a functionality of 3.5 and a viscosity of 300-600 cps at 23°C.

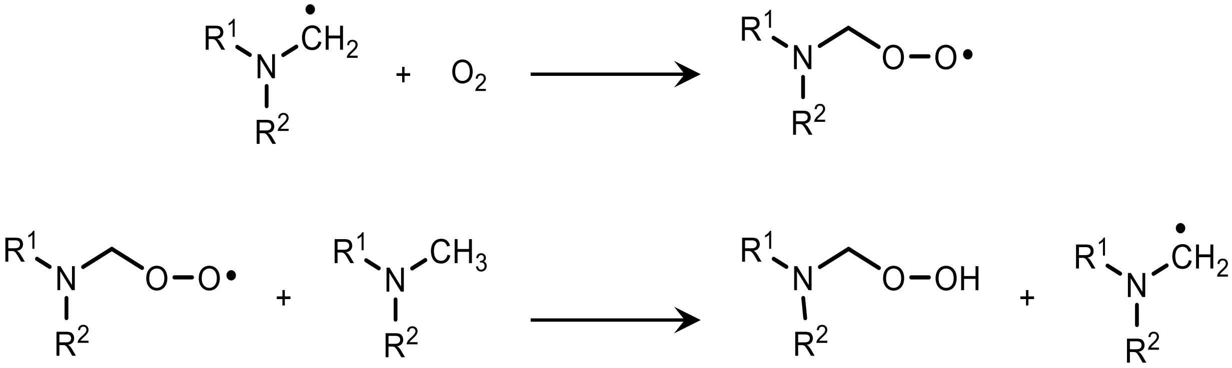

Figure 1. Mechanism of amino acrylates to control oxygen at the surface

2. Experimental

To investigate the performance properties of BPA-free (B-1) resin in comparison to epoxy acrylate (EA-1), the oligomers were compared in a minimally formulated OPV, and in OPVs with formulations shown in **Tables 2** and **3**. In both cases, performance was evaluated with and without amino acrylate.

The OPV formulations were made up of ethoxylated trimethylolpropane triacrylate and tripropylene glycol diacrylate. A mixture of photoinitiator blend consisting of BAPO (Bis acylphosphine oxide), liquid MAPO (mono acylphosphine oxide) and α-hydroxy ketone (AHK) were used for the study. A higher functional, low viscosity amino acrylate AA-3 was used during this study to investigate the impact of amino acrylate on performance properties of OPV. Properties such as viscosity, reactivity, adhesion, chemical and scratch resistance were used to compare the properties of OPV containing BPA and BPA-free formulations.

Materials	**% Component**	
	wo. AA-3	**w. AA-3**
Oligomer (B-1 / EA-1)	95	50
AA-3	-	45
Benzophenone + AHK (1:1)	5	5
Total	100	100

Table 2. Oligomer with and without amino acrylate

Materials	% Component	
	wo. AA-3	w. AA-3
Oligomer (B-1 / EA-1)	40	40
Ethoxylated TMPTA	30	25
TPGDA	20	15
AA-3	-	10
BAPO, MAPO, AHK	10	10
Total	100	100

Table 3. Overprint varnish formula with and without amino acrylate

The mixtures were heated in a 60°C oven and mixed well using a speed mixer at 2500 rpm for 2 minutes. Drawdowns were made using a #2 K rod (~ 12 μm film thickness) over both Leneta card N2A-3 and various plastic substrates. Substrates were cured using Heraeus HP-6/LC-6, (DRS-10/12, P/N SC61469DRS) Fusion 300 Watts/in D or the H lamp at varying % power and at a belt speed of 77 feet / min. The cure speed is reported as 1/exposure (cm^2/J), measured using power puck #8379 from EIT. Cure was determined by rubbing a cotton Q-tip stick aggressively over the cured surface on a polycarbonate or Leneta (N2A-3) substrate. Each time a new uncured drawdown was used and UV cured at a given belt speed, until no smudge was observed. A 610 Tape adhesion peel test was done on the cured ink after conditioning 16 hours at room temperature. Chemical resistance was done via MEK (methyl ethyl ketone) double rubs with a cheese cloth wrapped over a rounded hammer side. Scratch testing was carried out using a wooden tongue depressor by sliding over wide variety of substrates at an angle of 45°.

3. Results

3.1 Unformulated

To examine the cure speed and performance properties of BPA-free (B-1) oligomer in comparison to an epoxy acrylate (EA-1), a simple blend consisting of 95% oligomer and 5% photoinitiator was made with and without amino acrylate AA-3 (**Table 2**). A photoinitiator blend consisting of 1:1 benzophenone and α-hydroxyketone (AHK) was used for initial screening. **Figure 2** shows the viscosity and reactivity profile for formulations with and without amino acrylate AA-3. We found that the cure speed of B-1 is significantly improved with the addition of amino acrylate at 45% compared to nominal increase in formulation containing epoxy acrylate, **Figure 2**. The performance properties such as adhesion, scratch and chemical resistance were also evaluated over plastic substrates: polyvinyl chloride (PVC) and polycarbonate (PC) and the average values were plotted for the two oligomeric formulas. Overall, we observed that average adhesion over plastic substrate is better with BPA-free than the formulations containing epoxy acrylate EA-1 as depicted in **Figure 3**. Although the presence of amino acrylate in epoxy acrylate formulation seems to improve adhesion, the improvement is not as adequate and is also substrate dependent in epoxy-based formulation compared to BPA-free formulations. Scratch resistance, although better, is influenced to a lesser degree in epoxy-based formulation, but shows improvement in BPA-free system in the presence of amino acrylates. The 60° gloss is slightly higher for epoxy acrylate based formulation compared to BPA-free. Whereas chemical resistance evaluated as MEK double rubs is similar for the two oligomers and trends to be lower in formulations containing amino acrylates, **Figure 4**.

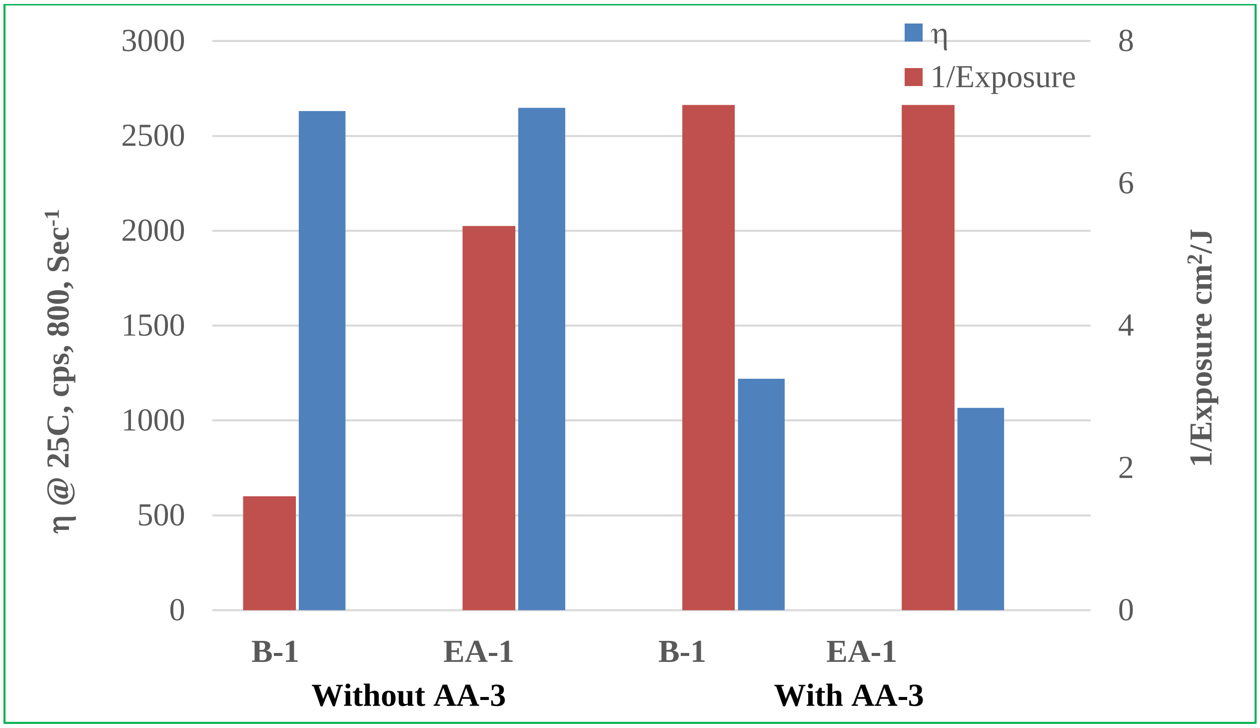

Figure 2. Viscosity and reactivity profile of oligomers with and without amino acrylate

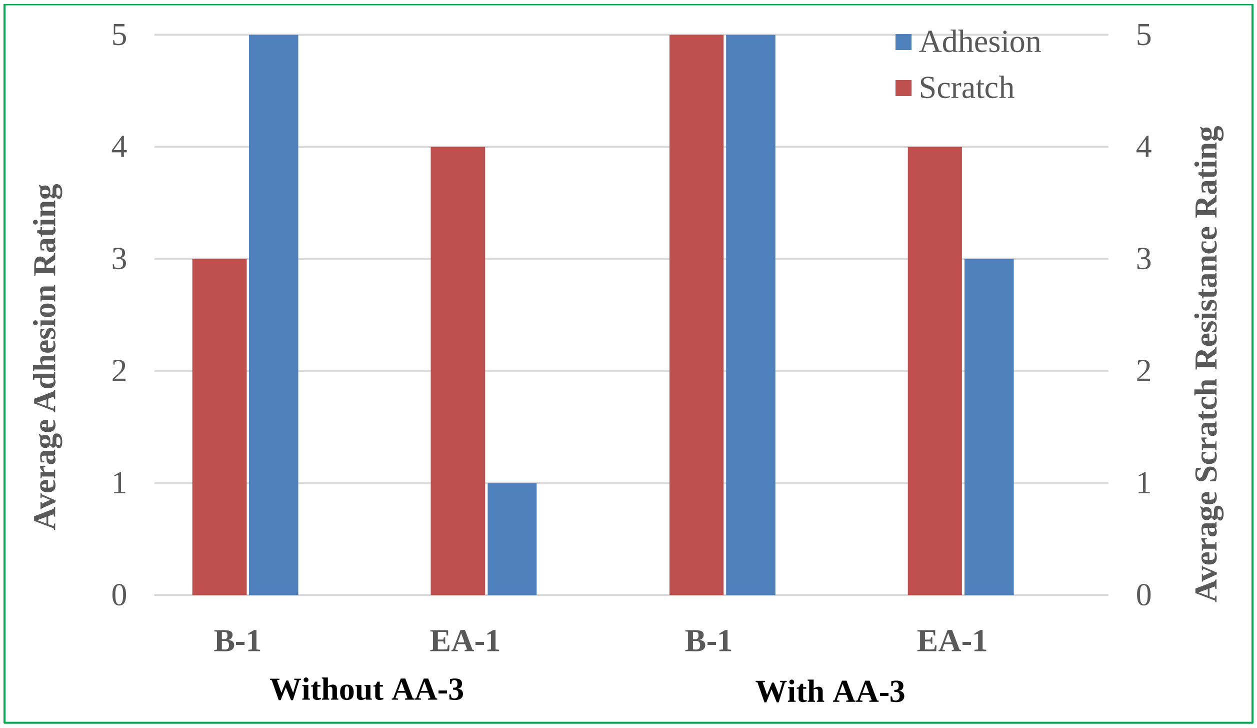

Figure 3. Influence of amino acrylates on adhesion and scratch resistance in B-1 and EA-1

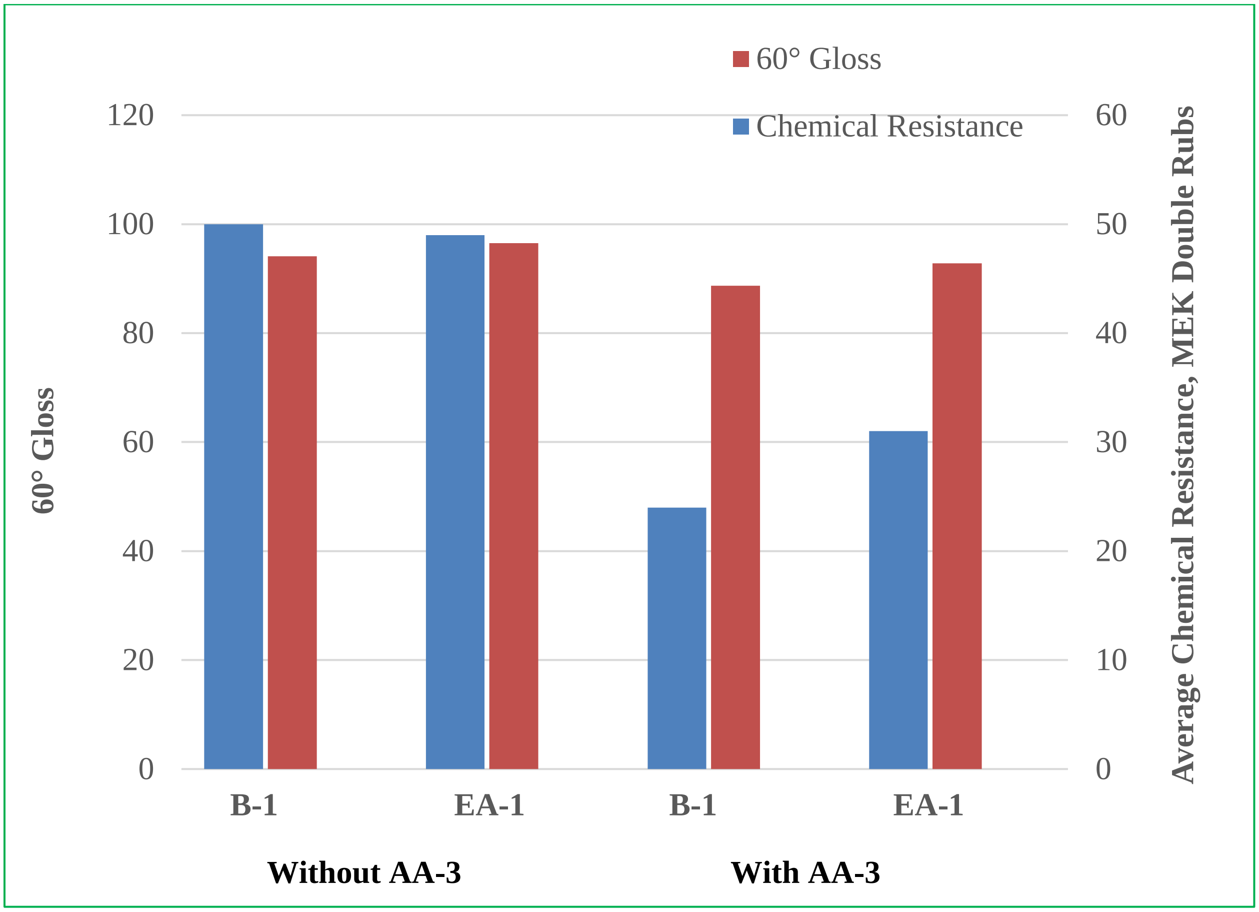

Figure 4. Influence of amino acrylates on 60° gloss and chemical resistance in B-1 and EA-1

3.2 OPV Formulations

OPV formulations shown in **Table 3** were also evaluated. The properties of formulations based on BPA-free oligomer B-1 with and without amino acrylates were compared to the properties of OPV derived from BPA-based epoxy acrylate. OPV reactivity, adhesion, and chemical resistance were compared and are shown in **Figures 5** and **6**, respectively. For this study, the OPV viscosity was maintained at < 250 cps. Drawdowns were made with #2 rod, which should yield a coating thickness of 10 - 12 µm over polycarbonate substrate. In **Figure 5**, we see that the cure speed of B-1 based formulations is marginally slower than the formulation based on EA-1, upon curing with D lamp. Addition of amino acrylate has a nominal influence on the cure speed compared to earlier formulas, as seen in **Figure 2**, for both B-1 and EA-1 based formulations. The difference in cure speed between the two formulations, as shown in **Figure 2** vs. **Figure 5**, can largely be attributed to the slower curing nature of the formula derived from ethoxylated trimethylolpropane triacrylate and tripropylene glycol diacrylate and the lower level of amino acrylate used herein as well as the lamp type used during cure. Both adhesion and chemical resistance properties were also evaluated upon cure over polycarbonate (PC), polyvinyl chloride (PVC), polyester (PET) and biaxially oriented polypropylene (BOPP) substrates. A 610 Tape adhesion test over these substrates revealed that the adhesion is largely substrate dependent.

Although adhesion over PC and PET was best with OPVs derived from B-1 oligomer under optimum cure speed conditions, the adhesion over PVC and BOPP was exposure dependent, requiring higher energy density. Although amino acrylate in B-1 based formulation improves adhesion over PVC under optimum cure speed conditions, adhesion over BOPP still requires higher exposure. However, irrespective of the amino acrylate in EA-1 based formulation or the exposure level, the adhesion is seemingly deficient over BOPP. Chemical resistance appears to be substrate dependent. The overall average rating is not significantly different for OPVs derived from these oligomers regardless of the presence of amino acrylate. This is shown in **Figure 6**.

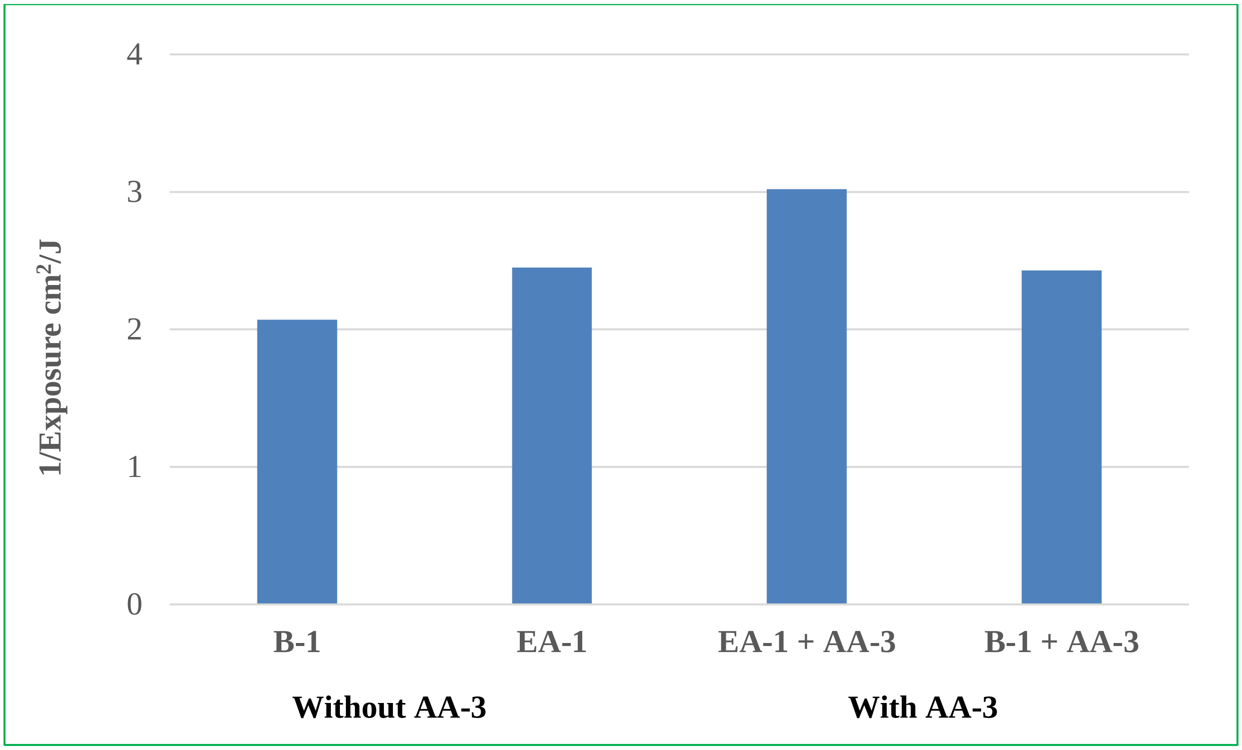

Figure 5. Reactivity profile of OPVs using EA-1 vs. B-1 with and without amino acrylate

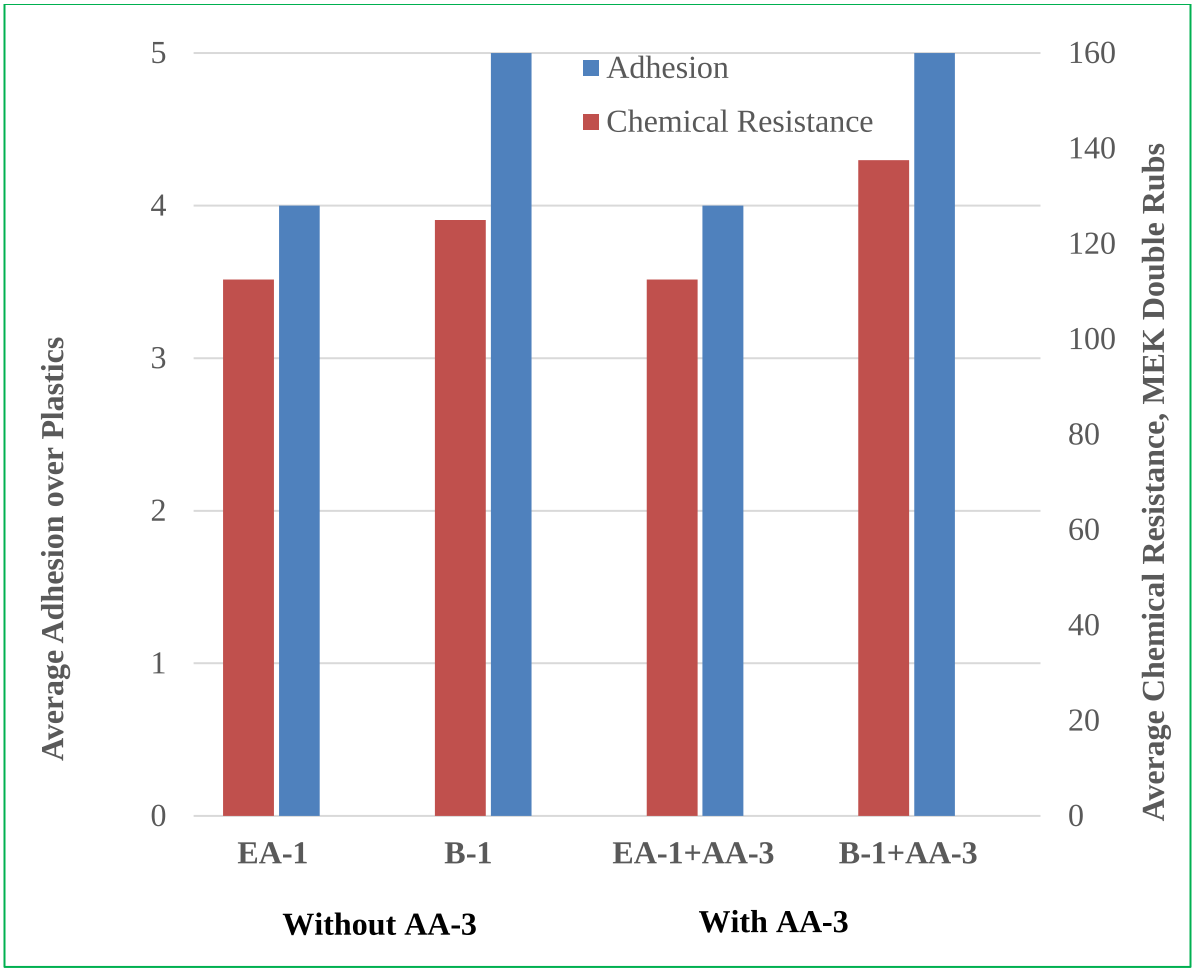

Figure 6. Properties of overprint varnishes with EA-1 & B-1 w & wo. amino acrylate

5. Conclusions

For packaging applications, BPA-free chemistry matching the performance of traditional BPA-containing epoxy acrylate formulations is desirable. Based on this study, we see that in presence of amino acrylate, cure speed of BPA-free oligomer is significantly improved. Similarly, the effect of lamp selection in OPVs is also important during cure as shown in **Figures 2** and **5**. This study is currently being utilized to evaluate the properties of pigmented flexographic inks derived from BPA-free B-1, and its comparison to a BPA-based epoxy acrylate EA-1, and will be the subject of the presentation at RadTech 2018.

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