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Reactive acrylic copolymers for use in low extractable coatings

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INTRODUCTION

Industrial coatings play an important role in many of the products used in our everyday life. These coatings may be solvent-based, waterborne, powder, or radiation cured just to name a few. Of these coating types, waterborne is the most widely used, followed by solvent-based, powder, and lastly radiation cured.¹ With growing regulatory pressure to reduce/eliminate VOCs, 100% solids UV/EB radiation-cured coatings have become a popular alternative to solvent-based coatings. When comparing the properties between the two coating types, both can be formulated to create scratch resistant coatings with high hardness. The same cannot be said when formulating a hard and flexible coating, however. Solvent-based coatings have the advantage of using high molecular weight polymers which can provide both hardness and flexibility while UV/EB coatings are typically comprised of monomers and oligomers which have a much lower molecular weight. In addition, the application viscosity for 100% solids coatings tends to limit formulations in terms of the concentration of oligomer being used, which in the context of UV/EB formulations is the closest component to a “polymeric” material.

Another factor to consider when transitioning to a UV system is the need for a photoinitiator. Photoinitiators are necessary to initiate the polymerization reaction once exposed to UV light. In the last couple of years, the UV coatings industry has faced its own regulatory challenges in regards to the reclassification of many common photoinitiators to substances of very high concern. While there are some coating markets where the migration of photoinitiators and subsequently their classification is not a concern, there are many markets that are impacted by these regulatory changes.

One way to mitigate the likelihood of a photoinitiator migrating out of a coating is to bind the initiating species to a polymeric or oligomeric backbone so that it becomes part of the cured network. Given that these “polymeric” initiators will be used in formulations at higher weight percentages than small molecule photoinitiators, it is important to choose polymers/oligomers that enhance the coating’s performance. As noted above, traditional acrylate monomers and oligomers can be used to formulate a wide variety of coatings; however, balancing hardness and flexibility is a challenge. Acrylic copolymers and acrylated acrylics (Ac-Acs) can be used in UV/EB systems as both inert and reactive resins (respectively) to reduce shrinkage and increase flexibility. For the purpose of this paper, an overview of the performance properties of acrylic copolymers which have initiating species grafted onto the backbone will be discussed.

MATERIALS AND EXPERIMENTAL METHODS

Acrylic Copolymer Design

Acrylic copolymers, as the name suggests, are polymers composed of at least two acrylate monomers. The properties of these polymers are governed by the properties of the individual monomers, along with the molecular weight of the polymer. A typical acrylic copolymer will use a combination of high and low glass transition temperature (T_g) monomers to tune the T_g of the polymer, which in turn can affect the hardness of the cured coating. In terms of molecular weight, a copolymer with a high molecular weight is likely to be more flexible than a lower molecular weight analog. While this may make higher molecular weight copolymers appear more desirable, it is important to remember too high of a molecular weight will impact their solubility in a 100% solids UV/EB formulation.

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All these factors were taken into consideration when designing the copolymer backbone. In order to determine the effect of backbone structure on the coating properties, five monomers with differing glass transition temperatures were used to synthesize a variety of copolymers with T_g values ranging from 40°C to 70°C. The molecular weights of the copolymers were also kept constant ($M_n \sim 30,000$ g/mol). Considering that the migration of photo-initiation species should be minimized, a Norrish type II initiator (benzophenone-based) was chosen as the chromophore to bind into the polymer. Norrish type II initiators only generate one radical upon exposure to UV, unlike Norrish Type I initiators which generate two radicals and can have more complex photo-byproducts. The benzophenone-based chromophore was reacted into the polymer backbones at 4 wt% so that once the reactive acrylic copolymers were diluted with 50% monomer, the concentration of chromophore was still high enough to cure a thin film.

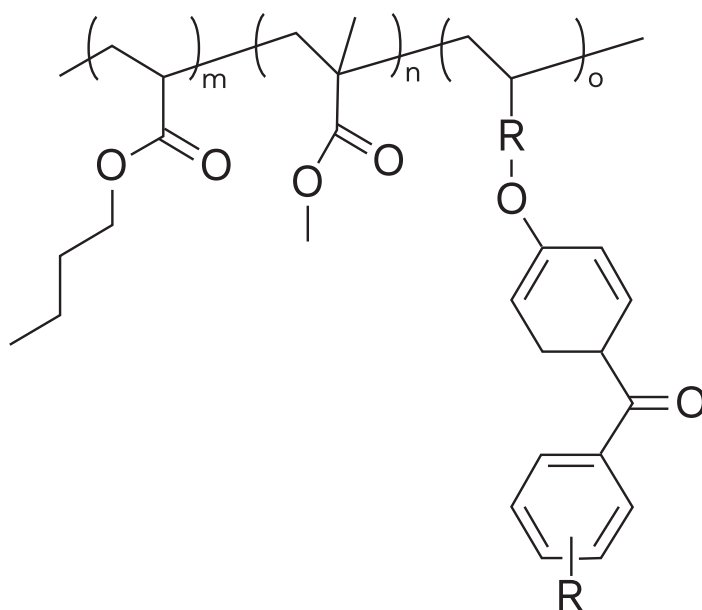


Figure 1: Example of acrylic copolymer with pendant chromophore

T_g	→			
		IBOA	MMA	IBOMA
↓	BA	RACP-1	RACP-2	RACP-3
	BMA	RACP-4	RACP-5	RACP-6

Table 1: Monomer combinations for reactive copolymer backbones

Table 1 shows the different monomer combinations that were used to synthesize the reactive acrylic copolymers (RACPs). The ratio of co-monomers needed to achieve the target T_g was determined using the Fox equation and consequently, each copolymer has different monomer concentrations. For example, a higher concentration of IBOA was used to make RACP-1 with a T_g of 70°C compared to the concentration of IBOA used to make RACP-1 with a T_g of 40°C. Given that these copolymers are solid at room temperature, 50% TPGDA (tripropylene glycol diacrylate) was added to the copolymers to achieve a workable viscosity. Each sample was coated onto a bare aluminum panel and PET at 2 mils and cured using a microwave powered 300 W/in mercury lamp with 1 J/cm² of energy exposure. After conditioning for 24 hours, cross-hatch adhesion (ASTM D3359) and stain resistance was evaluated. For the stain resistance test, black permanent marker and mustard were applied to the coating for 1 hour and then wiped off with a dry paper towel (no cleaning solution or water used) before measuring the coating's delta E using a colorimeter.

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RESULTS AND DISCUSSION

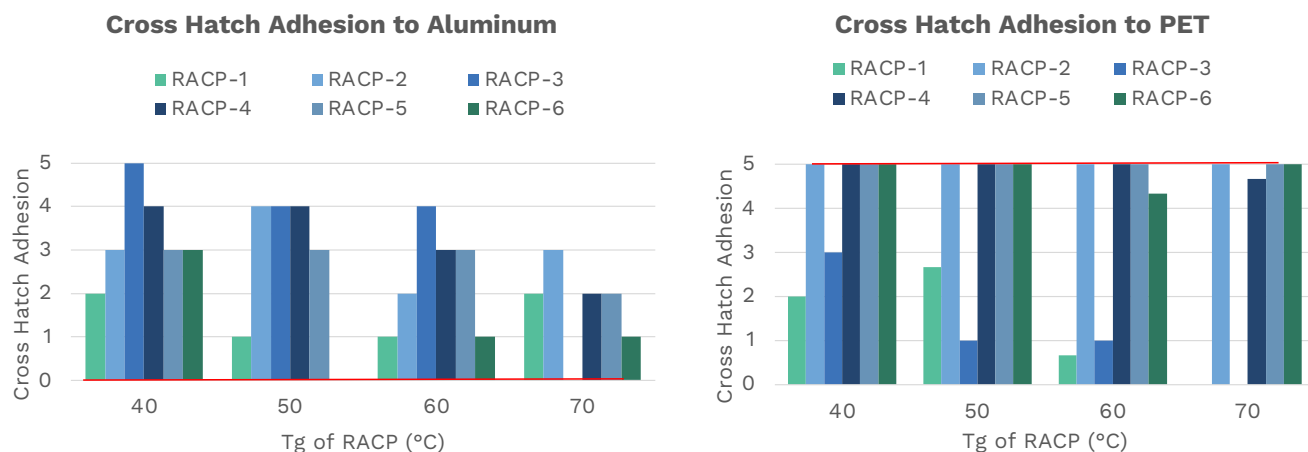


Figure 2: Cross Hatch Adhesion

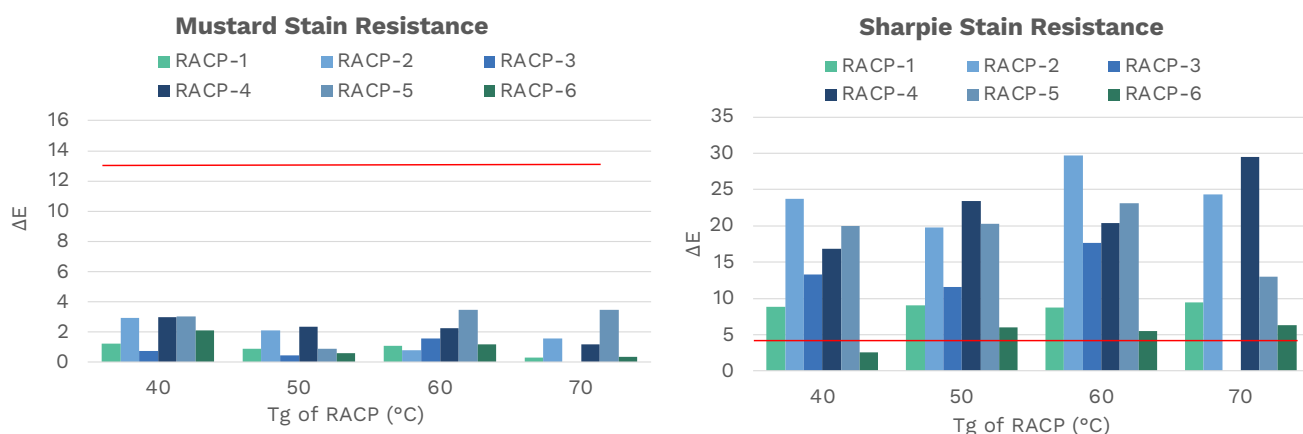


Figure 3: Stain Resistance

Figures 2 and 3 show the adhesion and stain resistance performance for all but one of the copolymers made. The 70°C Tg RACP-3 copolymer was not tested due to its insolubility in 50% TPGDA, resulting in a non-homogenous coating. Based on the results shown above it is difficult to make conclusive statements about the correlation between Tg and performance properties. Across all the Tg samples, all ranges of adhesion and stain resistance were observed. One might say that in terms of adhesion to aluminum, there is a very minor decrease in performance as the Tg increases which may be due to the more brittle nature of the copolymer. It is hard to make a similar observation for the coatings on PET since the cross-hatch penetrated both the coating and substrate, causing the PET to rip when pulling the tape off (coating stayed on the PET in most cases). Neat TPGDA was also tested as a control with 2% benzophenone to match the chromophore level of the diluted RACP systems and is denoted by the red benchmark line in the graphs. Compared to the control data, RACPs provide better adhesion to aluminum and comparable/better stain resistance than neat TPGDA. In general, it seems that the RACP monomer choice has a bigger impact on the properties than the ratio needed to achieve a certain Tg.

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Reactive Acrylic Copolymer for Adhesion

In an effort to minimize the number of samples, RACP-3 was chosen as the best candidate to continue to study adhesion to aluminum along with cold-rolled steel (CRS) in place of PET. A new set of RACP-3 copolymers with a wider spread of T_g targets (30°C, 60°C, and 90°C) was made to better parse out differences between samples. Since the goal is to understand the performance of RACPs as a low shrinkage/more flexible option to traditional high T_g acrylate oligomers, mandrel bend and König pendulum hardness were also added to the testing matrix. Initial testing of the acrylic copolymers showed poor adhesion to both aluminum and CRS. Upon further analysis, the newer batch of RACP-3 had a Mn much lower than the first batch. This may have resulted in a less flexible copolymer with lower adhesion to aluminum and CRS. In order to mitigate some of the brittleness, propylated neopentyl glycol diacrylate (PONPGDA) was substituted for the original diluting monomer (TPGDA). A comparison of the adhesion and hardness of the two systems across all T_g samples showed that adhesion was better in the PONPGDA samples across both substrates for the 30°C samples while the TPGDA samples did not show any conclusive trends.

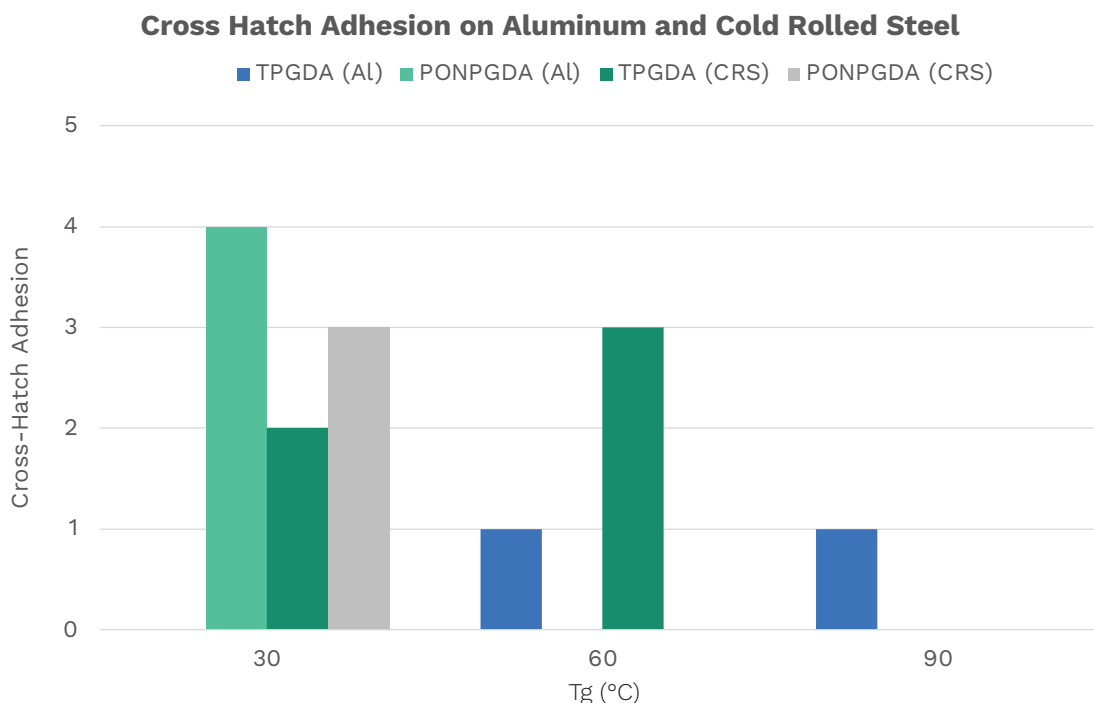


Figure 4: Adhesion to Aluminum and Cold Rolled Steel

Although adhesion slightly improved in the 30°C T_g system with PONPGDA, the samples did not pass mandrel bend. Given that the hardness values of the three different copolymer backbones (30°C, 60°C, and 90°C) all resulted in values over 100, it was decided that the focus would be placed on the 30°C copolymer as it showed the best adhesion and comparable hardness to the higher T_g samples. Further studies were conducted in which half of the PONPGDA monomer was substituted for either isobornyl acrylate (IBOA) or 3,3,5-trimethylcyclohexyl acrylate (TMCHA). Both of these systems had 100% adhesion to aluminum and cold rolled steel, along with improved mandrel bend results.

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Reactive Acrylic Copolymer for Stain Resistance

Similar to the study conducted for adhesion, one reactive copolymer was chosen to minimize the number of variables. In this case, RACP-1 was identified as the best candidate to evaluate for stain resistance due to its performance and raw material availability. The concentration of chromophore on the backbone was also increased from 4% to 6% to see if a higher degree of cross-linking would affect the stain resistance properties observed in the previous round. The reactive copolymer was benchmarked against two resins commonly used in flooring applications where stain resistance is needed.

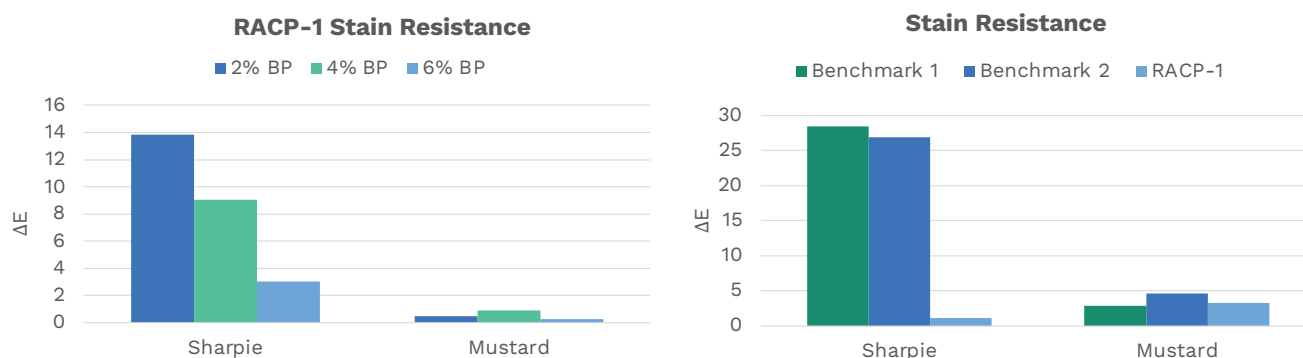


Figure 5: Stain Resistance

As can be seen from the graph on the left, the RACP-1 sample had better stain resistance compared to the two benchmark coatings. The effect of chromophore concentration can be seen in the graph on the right. Since the RACP-1 coatings are all diluted with 50% monomer, the final concentration of the chromophore is 1%, 2%, and 3% total. While one would expect that the samples with a higher concentration of chromophore would have a greater degree of cure, FTIR-ATR measurements at the coating surface showed double bond conversions greater than 90% for all samples. This shows that the stain resistance is related to the degree of cross-linking where the more photo-initiating sites present in the backbone to react, the more cross-linked the copolymer network.

CONCLUSION

Acrylic copolymers are great resins to use in UV/EB applications due to their low shrinkage and compatibility with acrylate monomers and oligomers. By adding reactive chromophore sites onto the backbone of the copolymer, one is able to reduce, if not eliminate, the migration of the photoinitiator and its by-products from the cured film. FTIR-ATR data has shown that acrylate conversion is not compromised in using reactive copolymers as the initiating species. Due to the high molecular weight of the copolymers, adhesion to metal substrates can be obtained without the use of traditional adhesion promoters. Similarly, the backbone of the copolymer can be tailored to impart properties such as stain resistance and high hardness. Since acrylic copolymers should be used as the main component in a formulation to maximize the concentration of chromophore, it is important to build as much functionality and performance into the copolymer design as possible. Future work will revolve around evaluating copolymers with higher concentrations of chromophore, along with performing extractables tests on reactive copolymer formulations compared to traditional UV formulations.

REFERENCES

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