Enabling energy curable adhesion through polymer design

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Introduction

The adhesion of energy curable coatings is a subject of great interest. This is particularly true for substrates that are low energy (i.e. plastics) or in the joining of substrates with different surface energies.[1] Advantages of energy curable coatings are that they are often very durable, can be rapidly applied, provide high scratch and mar resistance and do not contain volatile organic compounds (VOCs).

The challenges associated with energy curable coatings are often ones of adhesion. Often one formulation cannot work for multiple substrates, which means that formulators are left to design systems that work for a specific substrate.[2] This leads to inventory issues (multiple stock keeping units (SKUs)) as well as failure of formulations that are used for substrates where they are not intended.

Sometimes pre-treatment is required to get the energy curable coating to bond, adding capital and processing costs.[3] Additionally, lamination of surfaces after coating with an energy curable coating can be a significant challenge, much more significantly than with a solvent or water-based coating that has much more thermoplastic character and so can contribute to bond strength between the laminated layers.[4]

Adhesion is a complex mixture of physical and chemical forces, the understanding of which can lead to failure or success of a coating. Additionally, the components of the coating can impact performance as shrinkage rates, photoinitiator wavelength of activation and ductility of the film can play key roles in whether a film can withstand the rigors of the application for which it is designed.[4]

Typically, adhesion issues are addressed in three main ways. First, the surface is cleaned to ensure that there is a uniform surface for which the coating will be applied. Often this is done through a plasma or corona pre-treatment. The advantages of this is that the surface is uniform every time the coating is applied. The disadvantage is that the treatment adds costs, both from a capital expense but also from a processing standpoint.[5]

The second way to address adhesion issues is to increase the interaction of a formulation with the surface. This is typically done by adding a surfactant to match the surface tension of the substrate, allowing the maximum amount of surface contact between the substrate and the formulation prior to cure. The advantage of this method is that it can be designed specifically for the substrate, though that is also a disadvantage in that it is not always applicable to each substrate.[6]

The third way to address adhesion issues is to incorporate an adhesion promoter into the formulation. Adhesion promoters typically work by forming a chemical bridge between the coating and the substrate, the idea being that surfactants and pre-treatment address maximizing surface area while the adhesion promoter addresses actually getting the material to stick. Often these materials work very well, but again there are limitations based on the type of substrate for any one adhesion promoter.[7]

One way that is often talked about to enhance adhesion but not often quantified is the mechanical interlocking of the curable coating with the substrate. Every substrate – no matter how smooth – has some degree of surface roughness. If the coating can be driven down into the pores of the substrate, the surface area of the coating/substrate interface can be maximized, as shown in Figure 1. Additionally, shrinkage of the coating should then aid adhesion rather than being a detriment, as the film would tighten at the interlocking points rather than pulling away from the substrate.

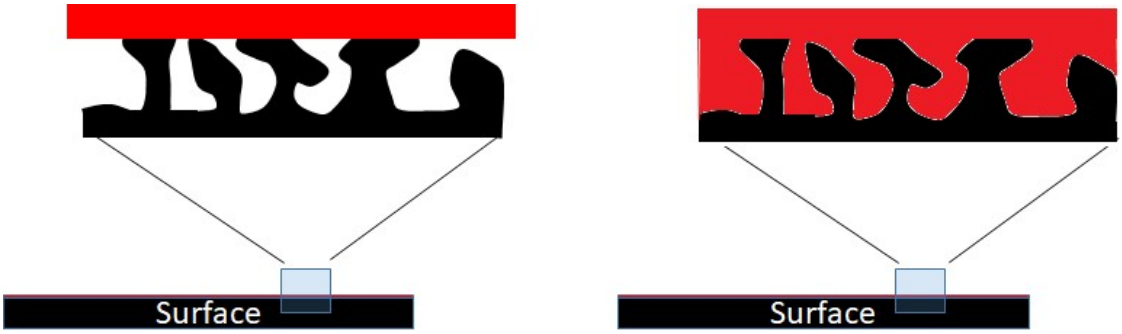

Figure 1. Image of a coating that is isolated to just the surface versus one that can utilize a mechanism of mechanical interlocking to increase adhesion

The issue with designing systems that utilize this interlocking mechanism is that there are opposing capillary forces that prevent coatings from infiltrating these "pores" fully.[8] Surfactants can be added to aid this infiltration, but often this isn't enough, even with precise rheological control of the film. It certainly is not universal as a surfactant is specific to the surface energy of the substrate.

The work in this paper shows a different mechanism for providing this interlocking mechanism. Here, we present evidence that it is possible to develop a polymeric material that will increase infiltration into various substrates based solely on the polymer architecture and design. We further present evidence that the force imparted by the polymer design is surface agnostic – i.e. it does not rely on surface energy or cleanliness to force its way into the pores of the substrate – and so gives a formulator significant latitude to make formulations that give good adhesion on multiple substrates.

Experimental

Synthesis

The synthesis of functional copolymers was carried out according to US patent (US 9,441,123 B2).[9]. A mixture of methyl ethyl ketone (MEK), vinyl chloride-co-vinyl acetate-co-vinyl alcohol terpolymer (UMOH terpolymer), unsaturated aliphatic isocyanate (TMI), and dibutyltin dilaurate (95%) was charged to a 4-neck round bottom flask. The resulting mixture in the reaction flask was stirred under

nitrogen and warmed to 75°C. A solution of benzoyl peroxide (98%) and 2,3'-azobis(2-methylpropionitrile) (AIBN, 98%) in MEK was charged.

A first monomer mixture, consisting of TMI and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 98.5%) was added simultaneously to the reaction flask. A second monomer mixture, consisting of 2-hydroxyethyl acrylate (HEA, 96%) methyl methacrylate, and DMAEMA, was then added with the balance of the initiator component to the reaction flask. Small amounts of AIBN were then added and the reaction was allowed to run to 100% completion. The material was then suspended as a water-based emulsion or isolated as a powder for further application testing.

This synthesis method can be tailored to give brush-like copolymers with diverse functional groups in the polymer backbones and side chains. Different concentrations of the monomers were added to control the functionality in the resulting copolymers. The copolymers examined in this study consisted of ratios of 13.5% and 27% branching to backbone.

Surface Force Characterization

Surface tension and contact angle measurements were conducted using an Attension Theta surface tensiometer. Surface tension measurements were conducted using the pendant drop method with a Teflon pipette tip to minimize any surface interactions between the solution and the tip. Contact angle measurements were conducted on injection-molded polyethylene terephthalate (PET) chips, with the results reported an average of measurements of droplets at three different locations. Figure 2 shows the surface tension and contact angle of the branched polymers in emulsion form compared to a linear polymer with amine functionality at a similar ratio.

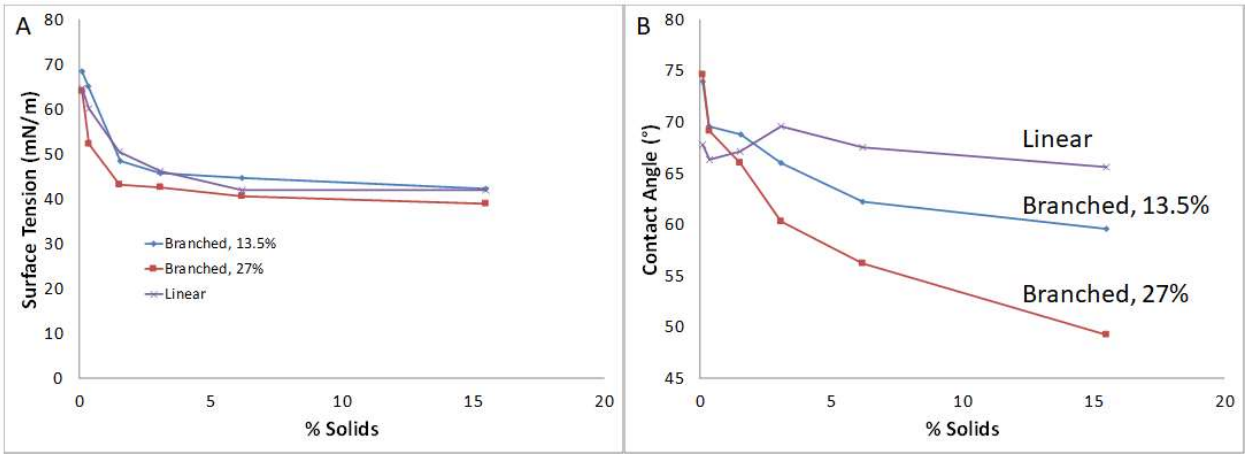

Figure 2. Surface tension (Figure 2A) of the branched resins are similar to a linear material with the same functional groups while their contact angle on PET (Figure 2B) is significantly lower and decreases with increased branching.

Figure 2 shows that the surface tensions of the branched polymers and linear polymer are virtually identical as the polymer concentration in water is changed. However, there is a marked difference between the contact angles of each of these components when deposited onto PET chips.

Because surface tension is a physical property measurement while contact angle is an application-specific measurement, this suggests that there is a difference between the way the resins act

with themselves and when they are put on a surface, with the branched polymers more adept at wetting out a surface.

Indeed, one observation made during the surface tension measurements was that when using a polypropylene tip for the measurements, the branched polymers would not form a droplet, but would rather migrate up the pipette tip. That was the reasoning for using a Teflon tip for the measurements and suggests that there is a non-surface tension-related force generated by the branching.

Emulsion Application Testing

While not energy curable specific, application testing of these materials as emulsions does give some insight to their versatility as well as the properties brought to bear by the branched architecture. For the first of these tests, emulsions were mixed with a paraffin wax containing a carbon black colorant above the melt temperature of the wax (130ºC). The 13.5% branched polymer and the linear polymer were incorporated into the wax at 10 weight percent solids and the water was evaporated off. The wax was then cast into a writing utensil and the resulting samples were compared to wax containing no polymer.

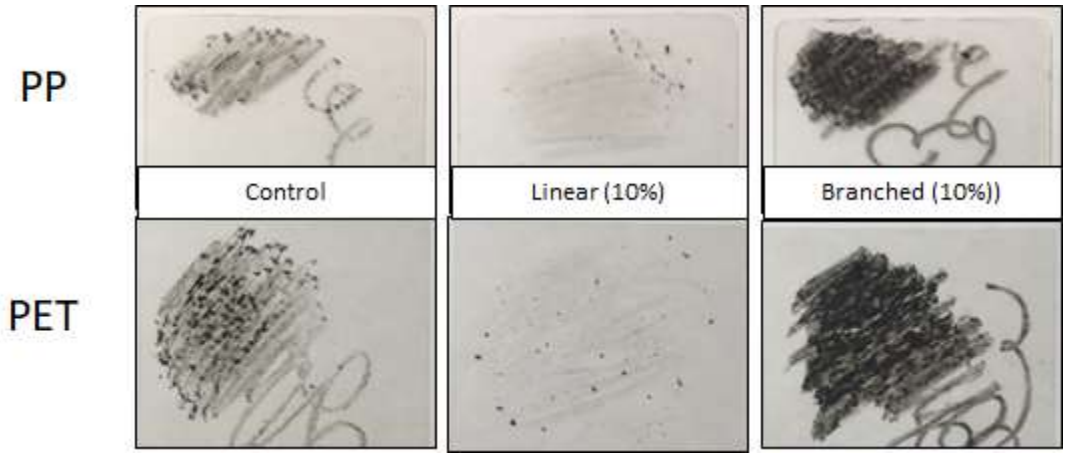

Figure 3. Comparison of surface adhesion of colored paraffin wax with incorporation of linear (Figure 3B) and branched (Figure 3C) polymers at 10% after incorporation into a colored paraffin wax.

Figure 3 shows the difference in efficacy between the control, linear polymer and branched polymer samples when rubbed on both polypropyelene and PET. This same effect was seen on steel, glass, high density polyethylene, an energy cured substrate and other smooth surfaces.

The control deposited on most surfaces decently, but then rubbed itself off as the sample was pressed into the surface with more force. The sample containing the linear polymer did not deposit on any surface well at all and rubbed off easily when more force was applied. The sample containing the branched polymer not only deposited on all of the surfaces easily, but it became darker as more pressure was applied.

This suggests that the polymer may be helping the wax adhere to the smooth surface, allowing it to build over time rather than being rubbed off with additional force. An interesting observation is that this adhesion appears to be surface agnostic. Because the effect is seen with all surfaces, this again

suggests this isn't a surface energy phenomenon, but rather something specific to the polymer being used.

This was further confirmed by adding the branched polymer (13.5%) to a polyvinyl alcohol adhesive at 10% solids loading. The same mass of adhesive with and without the branched polymer was applied to a glass slide and then an injection-molded polypropylene chip was pressed on top of the glass at a controlled pressure for 24 hours.

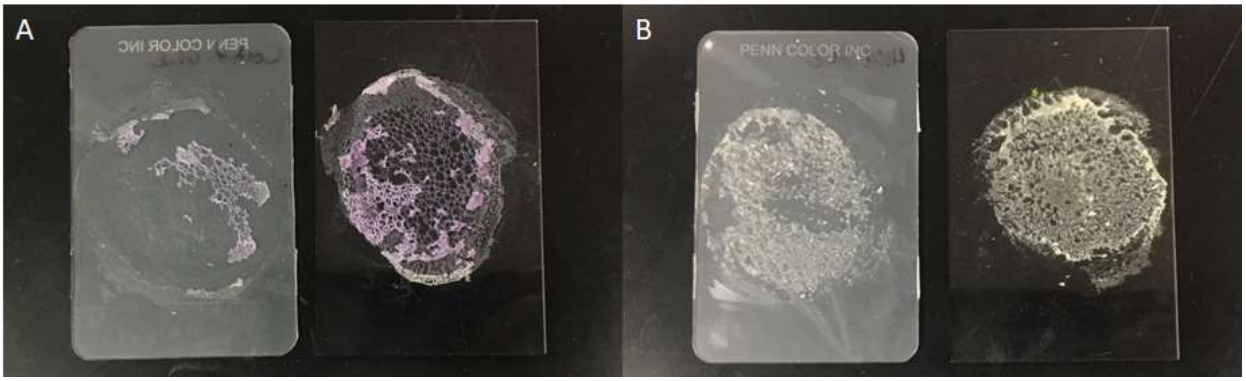

Figure 4. Adhesive failure (Figure 4A) vs. cohesive failure (Figure 4B) of a polyvinyl alcohol adhesive with (B) and without (A) incorporation of the branched polymer (10%) between glass and polypropylene substrates.

Figure 4 shows that the control sample had an adhesive failure, as after the samples are pulled apart, the majority of the adhesive is only on the glass slide. However, the incorporation of the branched polymer to the adhesive changes that to a cohesive failure where the actual glue is failing, rather than the adhesion to the substrate. This is clearly illustrated by the adhesive remaining on both the polypropylene and glass surfaces.

Energy Curable Application Testing

The powder version of the branched polymer was incorporated into energy curable formulations to test adhesion to various substrates, specifically PET and a previously cured UV coating. Solubility of the powder was limited (<1%) in various common energy curable components unless it was first solubilized in a low molecular weight monomer such as butyl methacrylate (BMA, 99.9%, TCI America) or 1,6-hexanediol diacrylate (HDODA, technical grade 80%, Millipore Sigma). Once the material was solubilized into these monomers, it could easily be incorporated into various formulations in excess of 15 weight percent.

In the first example, the branched polymer was put into a proprietary UV curable formula consisting of 15 wt% branched polymer. The proprietary formula does contain a difunctional urethane acrylate, which was substituted out for the branched polymer. The formulation was tinted with a red UV-compatible pigment dispersion to enhance the ability to see the effect of the polymer in the application tests.

Films of the formulas – a control without the polymer and a sample containing the polymer – were drawn-down onto PET films using a number 26 wet film applicator rod. The film was then UV-cured by passing through a UV lamp at 40 fpm five times. The resulting films were shiny and hard, with no material

transfer or tackiness upon touching. The films were then tested using crosshatch tests, following the methods described in ASTM D3359.

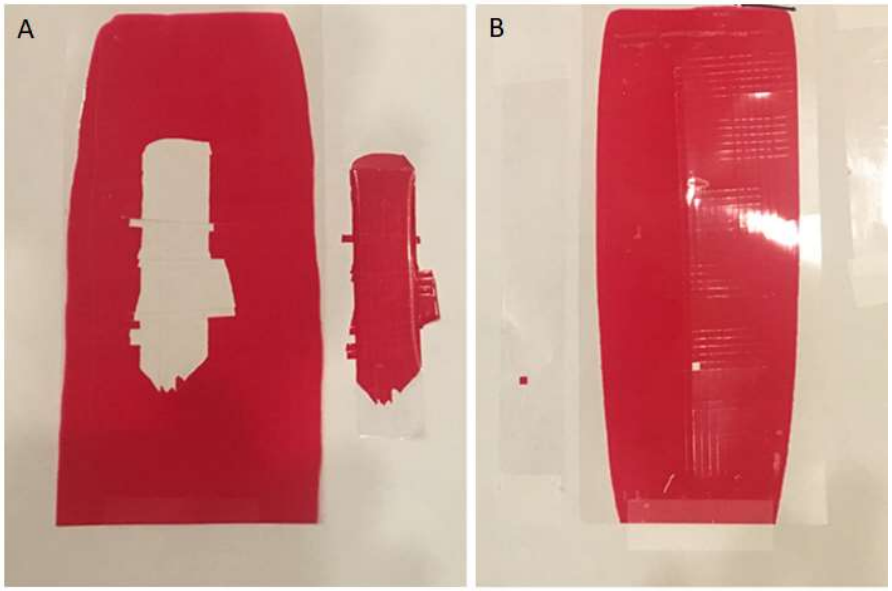

Figure 5. Significant removal of energy curable film using crosshatch test (Figure 5A) is completely eliminated on a PET film by incorporation of branched polymer (Figure 5B) into formulation.

Figure 5 shows the crosshatch results from these tests and the enhancement of the adhesion with the branched polymer added. There is complete adhesive failure of the film that does not contain the branched polymer powder. However, the performance with the branched polymer is considerably better, only having one small square removed from the PET film.

The films were then examined after being cross-sectioned using a Zeiss Axio Imager.A2m optical microscope with an Axiocam 305 color camera at 200X magnification. Following cross-sectioning, the films were stood on end and clamped in place to get a full view of the interface between the film and the surface.

Figure 6 shows these cross-sections, and what is apparent is that there is delamination of the coatings from the PET film in both situations (the black space between the white film and the red coating). However, for the sample containing the branched polymer, there are places where delamination did not take place. Additionally, that sample has a much more variable interface than the control sample. This suggests that the branched polymer may be enhancing adhesion through the mechanical interlocking mechanism discussed above.

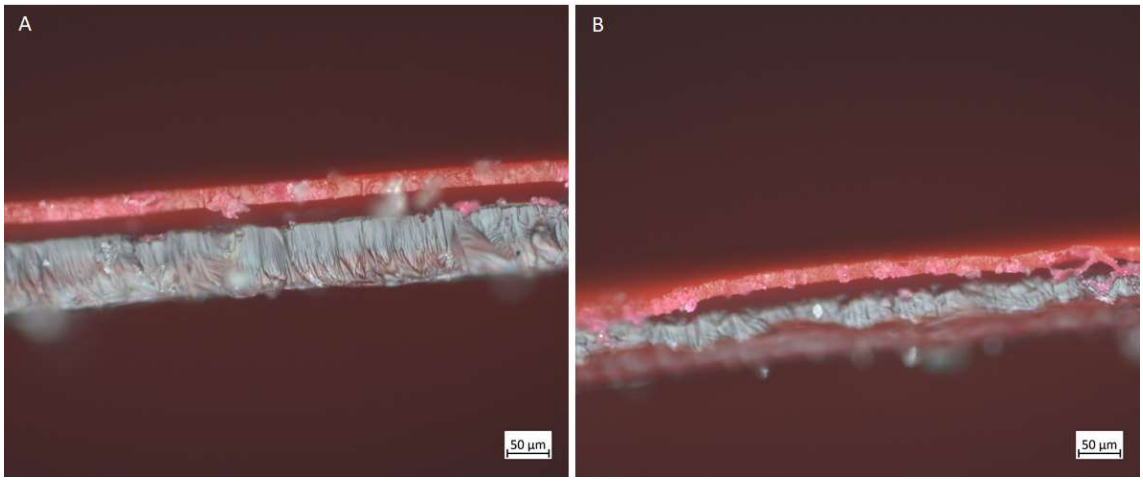

Figure 6. Cross-section of energy curable film on PET shows a uniform film at the point of delamination (Figure 6A) vs. the cross-section of the formulation with the branched polymer added (Figure 6B), which shows much more roughness and areas where delamination does not occur.

The branched polymer was then added at 1.8 wt % to a proprietary black UV curable formulation. This coating needed to be able to stick to a previously cured UV coating containing a silicone acrylate to increase slip. In this case, a white coating was used to ensure high levels of contrast.

The white coating was drawn down on a glass substrate using a number 26 wet film applicator rod. The coating was then UV-cured by passing through a UV lamp at 40 fpm five times. The resulting coatings were shiny and hard, with no material transfer or tackiness upon touching. The black coating was applied in the same fashion after the white film was completely cured.

The black film was then tested for adhesion and scratch resistance using a pencil hardness tester, in accordance with ASTM D3363. The hardness of the pencil was slowly increased until a failure of the film occurred.

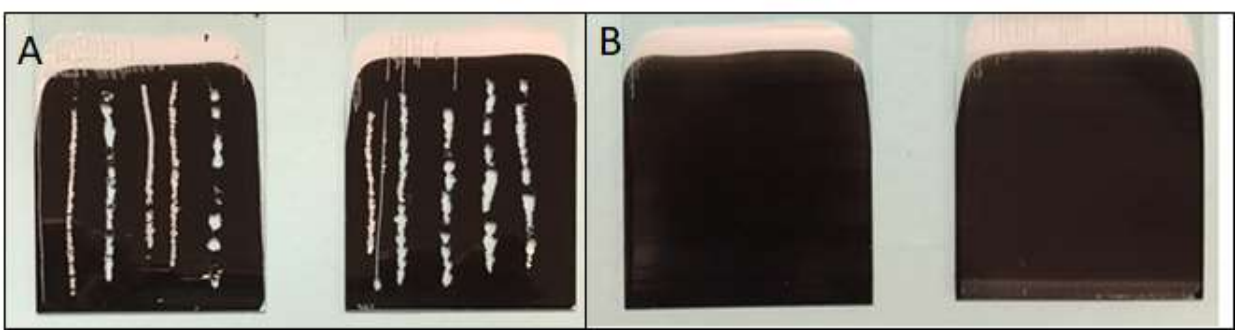

Figure 7. Energy curable black coating cured on top of an energy curable white containing a silicone acrylate, then tested using a pencil hardness tester (H) on films with the branched polymer absent (Figure 7A) and present (Figure 7B, 1.8%).

Figure 7 shows the effect of adding the branched polymer to the formulation, even at a small percentage. The cured black film shown in Figure 7A scratched easily with the H hardness pencil, uncovering the white coating underneath and sometimes even removing the white from the glass

directly. The cured black film shown in Figure 7B containing the branched polymer did not show any failures at the same H hardness level.

Conclusions

It has been shown that adhesion can be increased on multiple substrates for multiple formulations just through the incorporation of a branched polymer. The structure of the polymer and the degree of branching all play a role in the degree and ability of the polymer to aid adhesion. This increased adhesion has been seen from both a water-based emulsion of the polymer as well as the isolated polymer powder.

There is evidence that the material causes wetting in a way that is surface-tension independent, meaning that there is a force imparted by the polymer that aids wetting and surface roughness penetration regardless of the substrate. This allows the branched polymer to be utilized for both high and low energy substrates, and potentially to join surfaces with large surface energy differentials. Because of this – and microscopic evidence – we believe this increase in adhesion may be due to increased mechanical interlocking at the surface.

Particularly for energy curable coatings, there is visual evidence that cured films have more roughness when cross-sections are examined, indicating that the film has much more intimate contact than a typical energy curable coating. This provides a different mechanism for increasing adhesion than improved wetting through surfactants or chemical bonding through the addition of an adhesion promoter. This could be a powerful addition to a formulator's toolbox given the ability to take a formulation that fails catastrophically and make it perform to a potential customer's specifications.

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