LED Curable Dichroic Coatings Based on Structural Color Copolymers

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Introduction

Pursuing reduction of carbon emissions across myriad industrial products is an important initiative to combat climate change. An appealing (albeit historically difficult) method to reduce the carbon emissions is by innovating around the raw materials that form these products. Coatings and inks are not immune to these efforts, especially those with unique functionality where state-of-the-art optical effects or beneficial thermomechanical properties are desired. Coatings typically contain a solvent (water or petroleum based), resin, pigments, and other additives to optimize film performance. Once the coating is applied, curing ovens (commonly heated with natural gas) are used to evaporate the solvent and, optionally, drive the crosslinking chemistry of choice. When considering a cured coating, the difference between water vs high solids solvent-based technology seems to be minimal with their carbon emissions nearly equal, but with VOC reduction and improved safety of the former.[1] Powder coatings offer an even lower footprint, but surface finish is not acceptable in all cases. UV curable systems offer both a lower carbon footprint, desirable appearance, and excellent film properties. However, pigmentation is still required to impart color and these components carry significant environmental impact.

Analysis of a standard paint formulation reveals pigments and dyes are the highest constituent of carbon emissions ranging from 30% up to 60% of formulated coatings.[3] A novel alternative to traditional pigmentation is structural color based on brush block copolymer technology. Lifecycle analysis results indicate brush block copolymers have less than1/5th the carbon footprint of organic pigments preferred for their high chroma (Figure 1).[4] Given the importance of reducing carbon emissions associated with coatings, the benefit from the combination of 100% solids UV LED curing technologies and structural colors created with brush block copolymers seems to be an ideal choice.

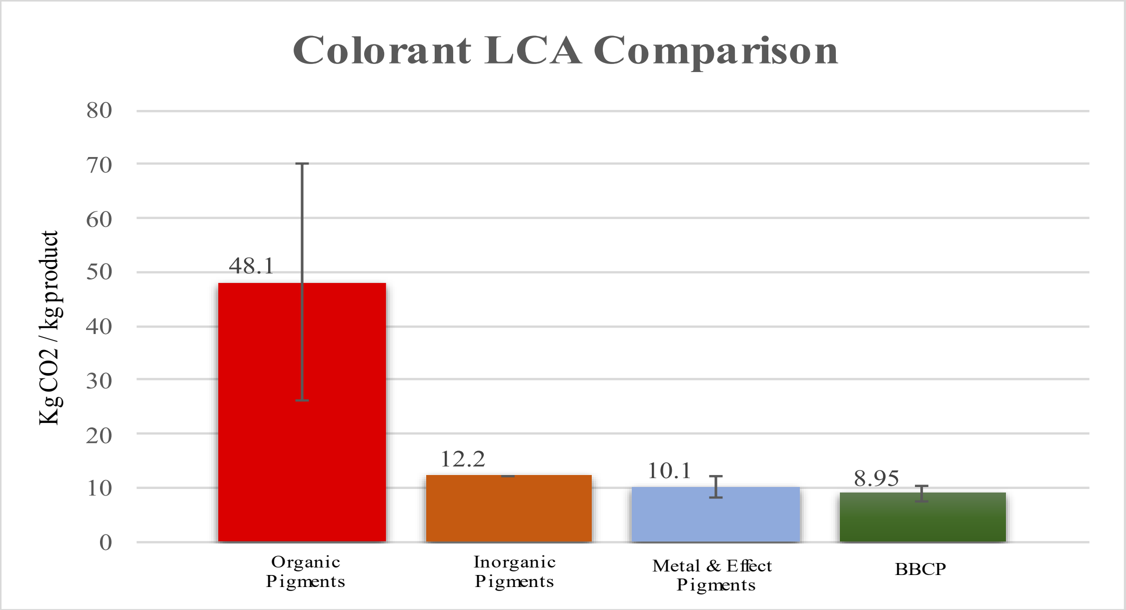

Figure 1. Lifecycle assessment (LCA) comparison of common pigment technologies and brush block copolymers.

Structural Color: From Nature to Brush Block Copolymers

Structural color can be found throughout nature in both biological and geological examples ranging from butterflies, beetle carapace, berries, as well as natural gemstones such as opal. The uniting feature across these various natural sources is the presence of small, periodic features that interact with light without relying on absorption as the primary color-generating phenomenon (Figure 2). Depending on the feature size, refractive index, and fidelity of the ordered nano- and micro-structure of the constituent materials, they can reflect wavelengths throughout the electromagnetic spectrum.

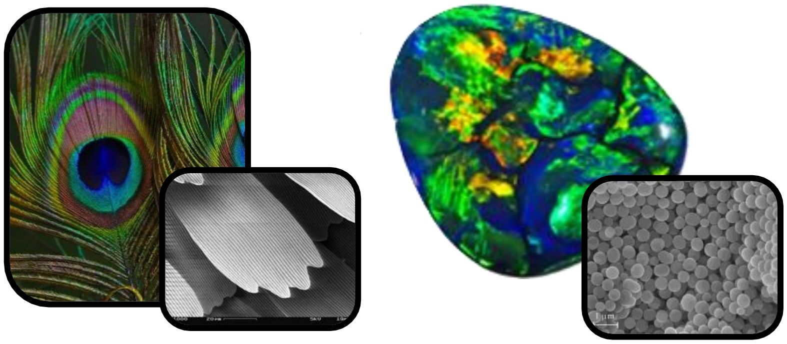

Figure 2. SEM images revealing small fine lamellar structure contained within peacock feather (left) and natural opal cross section SEM showing internal silica spheres approximately 500nm in diameter (right).

Brush block copolymers (BBCPs) have been studied for their unique ability to rapidly self-assemble to create one-dimensional phonic crystals, via formation of stable nanostructures, the most common of which is the lamellar morphology (Figure 3).[2] When properly designed these materials yield highly chromatic, dichroic coatings. Their reflected wavelength can be tuned to span the ultraviolet, visible, and near infrared ranges offering additional functional benefits such as lidar visibility and solar cooling. Previous coatings of BBCP have focused on solvent-based formulations to dissolve the copolymers and provide needed evaporative mobility to enable self-assembly and color formation before curing (Figure 4). This report presents the use of UV curable monomers to formulate structural color coatings using BBCP's without the need for evaporation to form color.

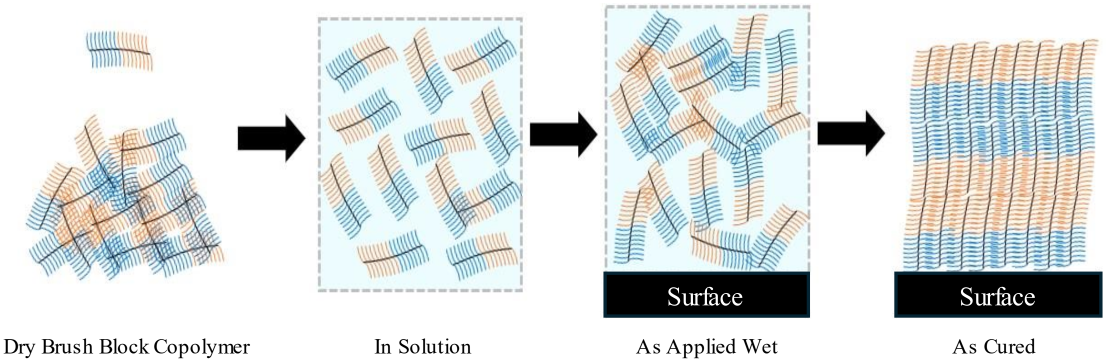

Figure 3. Illustration of evaporative brush block copolymer self-assembly process

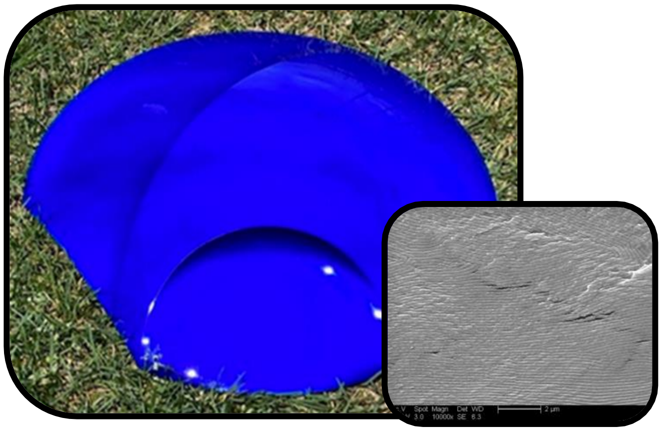

Figure 4. Spray painted panel demonstrating high chroma blue created with BBCP (left) and SEM cross section of cured BBCP coating (right), showing the lamellar structure created via the evaporative self-assembly process.

Structural Color Mixing: Wavelength Averaging

UV curable formulations are composed of mixtures of mono- and oligo-acrylates, pigments, additives, and photo initiators. When exposed to UV energy, the formulation instantly cures to form a durable coating. Pigmentation can be added in low concentrations if the UV light can penetrate the coating and initiate the free radial chain reaction for sufficient cure. BBCPs have sufficient solubility in common mono-, di- and tri-acrylates, and compatibility with oligomeric acrylates and inert fillers, to form a viable UV curing formulation. Visual observation of BBCP/acrylate solutions and dispersions during the mixing process demonstrate significant self-assembly, as evidenced by their highly opalescent appearance pre-deposition or curing. When applied using drawdown application, highly chromatic wet films are generated. Coatings with high cross-link density result in film shrinkage upon cure and compress the feature sizes, resulting in a shift to shorter reflected wavelengths compared to the wet colors. The reflected color can be modified by manipulating the polymer characteristics (i.e. molecular weight) and formulation components. As with naturally occurring structural color, small features reflect shorter wavelengths, and as the feature size increases, the reflected color transitions to longer wavelengths.

In addition to the environmental benefits of UV LED curable BBCP structural color coatings, the technology can generate many different colors from two inputs of identical chemical composition (but different molecular weight). Unlike additive or subtractive color mixing, the underlying framework is known as wavelength averaging: the reflected peak wavelength is determined by the average BBCP molecular weight or feature size formed in the formulation.

To evaluate this value proposition, representative formulations of approximately ~20% BBCP were made with low and high molecular weight BBCPs, with a blend of acrylate components to enable acceptable film flexibility for practical handling (Table 1). Individually, the cured films peak reflectance was measured to be 450 and 620nm, respectively. Cross blending of formulations to generate ratios ranging from 20-80% small brush formulation were made, applied by drawdown coating, and cured with a Phoseon 395nm LED UV light (dose = 200 mJ/cm^2).

Table 1. High and low molecular weight BBCP containing formulations.

Sample	BBCP Blend (low:high)	Lambda max (nm)	BBCP Loading (wt %)	HDDA (wt %)	BzA (wt %)	IsoA (wt %)	EtHA (wt %)	PI 1 (wt %)	PI 2 (wt %)
1	100:0	455	19.4	35.09	33.73	3.06	2.90	3.88	1.94
2	0:100	620	19.4	35.09	33.73	3.06	2.90	3.88	1.94

HDDA = hexanediol diacrylate, BzA = benzyl acrylate, IsoA = isodecyl acrylate, EtHA = 2-ethylhexyl acrylate, PI 1 = Omnirad 819, PI 2 = Esacure ONE

The films were characterized using an X-rite MAT-12 multi-angle spectrophotometer demonstrating high chromaticity and angle dependency. Of the six films coated, the resulting spectral data were normalized and are shown in Figure 5.

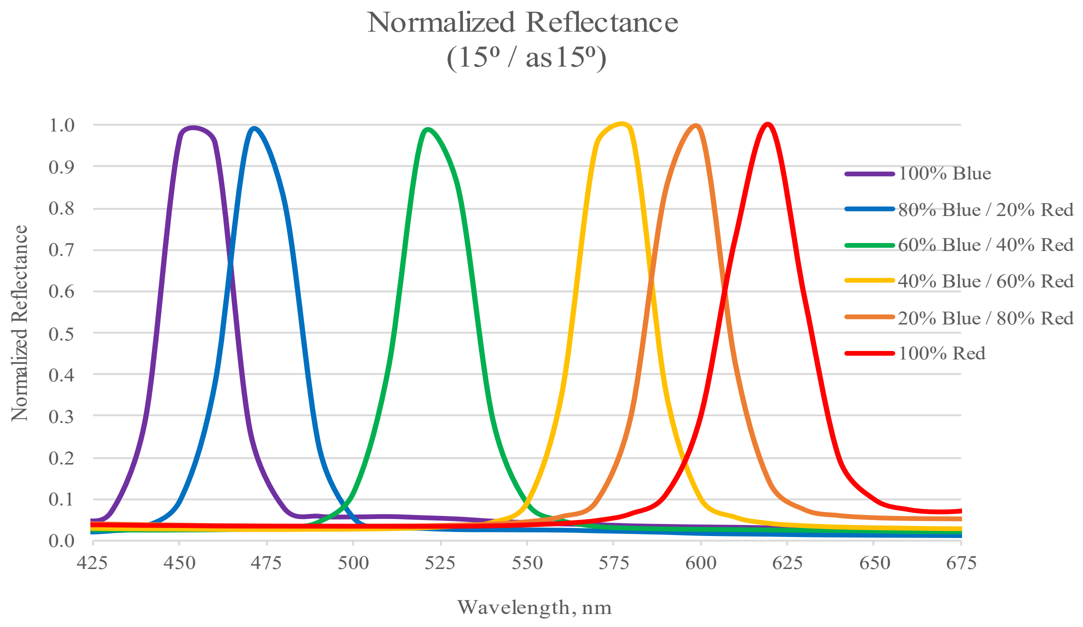

Figure 5. Normalized reflectance values measured at 15º/as15º configuration.

Although the combination of red and blue to create intermediate hues is surprising and not predicted by additive and subtractive color mixing theories, when considering the wavelength of maximum reflection, a strong linear correlation to the weight fraction of either red or blue can be seen as shown in Figure 6. The slight deviation from a perfectly linear trend is likely due to the lack of formulation fine tuning across the color spectrum. Individual improvements in the color quality can be unlocked by subtle recipe modification. This general relationship will no doubt prove useful when developing color match software for BBCP commercial applications.

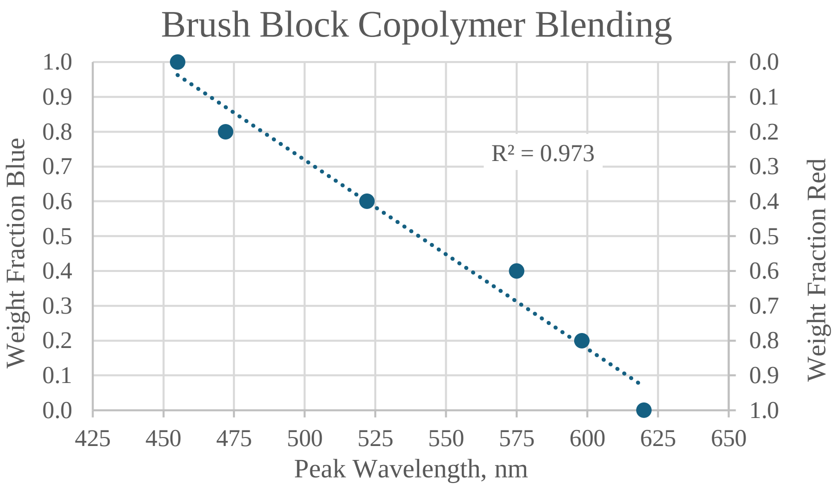

Figure 6. Plot of the peak wavelength of reflection for films with varying weight fractions of Blue (low molecular weight) and Red (high molecular weight) BBCP.

UV Curable Coatings: Dichroic (Angle Dependent) Coloration

In addition to the strong color saturation, BBCP based structural colors offer a dichroic, or color shift effect where the color changes with both illumination and observer angle. BBCP structural colors exhibit stronger saturation when viewed near the specular reflection. Of the eleven color measurements assessed with the MAT-12, of interest to assess interference color are the ones near specular, namely, 15/as15º, 15as-15º, 45/as15º and 45/as-15º shown in Figure 7. Additional analysis was made to evaluate the gonio-apparency of the coated films utilizing the interference angles associated with observations at 0º, 15º, 30º and 45º from normal as shown in Figure 8.

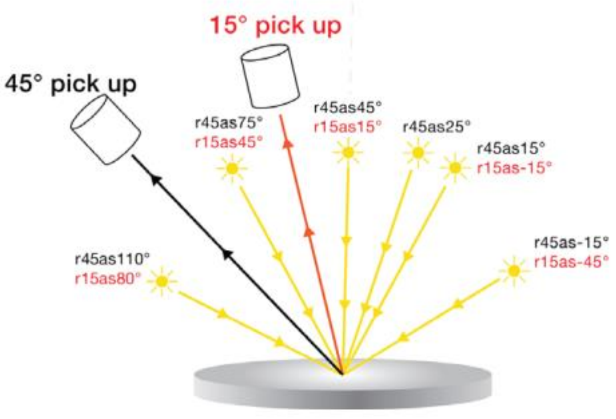

Figure 7. MAT-12 multi-angle spectrophotometer geometry courtesy of X-rite Inc.

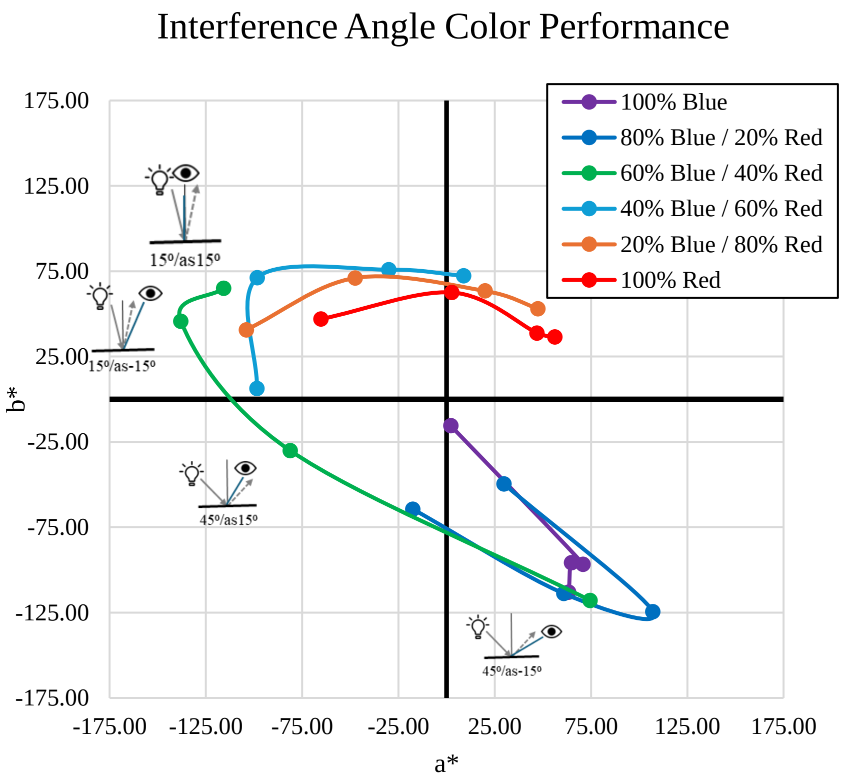

Figure 8. Interference colors as measured at 0º, 15º, 30º and 45º from normal. The 60% Blue / 40% Red formulation has been annotated for clarity.

The elliptical pattern observed for the a*b* color values characterize the range of color combinations visible from red-gold-green, gold-green-blue, green-teal-blue and blue-indigo-black, with the 100% Blue formulated color shifting into ultraviolet region. These color shifts offer new visual effects that are difficult to replicate by existing effect pigment technologies.

Conclusions

Drawing on inspiration from naturally occurring materials, BBCPs offer an appealing opportunity to industrialize structural color and reduce the environmental impact associated with traditional pigments and dyes. When combined with 100% solids LED UV curable technology, the fully cured films hold the potential for uncompromised performance and stunning visual effects. Further research into optimizing formulations for various industrial coating applications is warranted to further drive adoption of this technology and realize the full esthetic and environmental benefits it has to offer.

References

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