

Effect of Additives on the Color & Appearance of Plastics

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Abstract

The color and appearance of a formulation must be engineered just like any other desired thermal or mechanical property of the resin itself. The ability to achieve the desired color can be adversely affected by processing or the combination with modifiers and additives in the resin system. Even if colors can be achieved, other performance attributes such as UV stability, flammability or mechanical properties may be adversely affected as well. This paper looks at some of these color concerns.

Introduction

To many people, color is at best a necessary evil. The coloring process amounts to adding a contaminant (the colorant) to a perfectly good polymer system to achieve a color while reducing all other properties! This perception can be transformed into reality when color is an afterthought in the whole product development cycle. That cycle typically progresses as follows:

- 1) the customer has a problem
- 2) a new resin formulation is developed to solve it
- 3) the new resin (in natural, uncolored form) is molded and tested
- 4) the new resin indeed solves the problem
- 5) the customer now reports they need the resin in dark green
- 6) the color group formulates the dark green using three times the normal pigment loading
- 7) the new resin in dark green is molded and tested by the customer
- 8) the new resin in dark green no longer solves the problem due to strength and warpage issues
- 9) back to step 1!

Of course, all of this can be avoided if the color and appearance of the resin are engineered along with other desired thermal and mechanical properties. That way, when the desired engineering properties are met, so is the color (at least the closest achievable color anyway). Because one must also be aware that including the colorability of the resin early in the development process is no guarantee that all desired colors can be achieved. What this work will accomplish is to help define problems and limitations in achieving colors up front. And if there are limitations, this information can then be used with the customer to help select colors that are achievable without detrimental side effects.

None of this of course is new information. But it can be forgotten. The purpose of this paper is to present

information that unequivocally shows that color should not be an afterthought in the development cycle. Discussion will be focused on describing adverse effects on colorability attributed to the base polymer itself, other blended polymers, modifiers, additives and stabilizers. [Note: since this paper is written by a colorist, information will be presented in the spirit of the pure colorant being adulterated by the polymer system and all of its additives!]

Visual Color Perception Process

Before we can discuss color concerns in polymers and blends, it is important that the reader has an understanding of the visual color perception process. In order to see color, three things must exist: a light source, an object and an observer. For purposes of this paper, describing the light source and observer are not included other than to say we assume the light source contains all wavelengths (i.e., white light). The object in our case is an article molded from our colored resin. A beam of light reaches the surface of our object. A portion of the light is reflected due to the surface interface and is called the specular reflection or gloss component. The remainder of the light penetrates the surface of the object where it is modified through selective absorption, reflection, and scattering by the colorants, polymers and additives. Selective absorption and reflection by wavelength create color. For example, if an object absorbs all wavelengths of light other than blue, blue light will be reflected or transmitted and the object will appear blue.

Scattering occurs when the light beam contacts particles or regions within the polymer system that have an index of refractive which is different from that of the base polymer. The change in refractive index that the light beam encounters causes the light to be redirected and, if the index of refraction is increasing, to slow down. The index of refraction is a physical property of the substance. It is determined by the equation:

$$\frac{\sin \theta_1}{\sin \theta_2} = n,$$

where θ_1 and θ_2 are the angles formed by the incident ray and the refracted ray versus the normal as shown in Figure 1.

The index of refraction for a substance depends on the wavelength of incident light. This relationship is most often observed by refracting light with a prism. In a prism, the blue wavelengths of light are refracted more than the red region of the spectrum because of this function. The result is the obvious separation of wavelengths and our ability to see the individual colors of the spectrum. For

anisotropic crystals, the index of refraction also depends on the crystal axis on which the light is incident. For these materials, the index of refraction as a number is typically reported as an average value of the various axes.

If scattering occurs nearly equally at all wavelengths with no absorption, the object will look white. That is how titanium dioxide appears to impart its white color to objects – by scattering virtually all of the incident light. In mixtures of titanium dioxide and dark pigments such as carbon black, the index of refraction as a function of wavelength becomes apparent. Because the index of refraction for the titanium dioxide is higher for shorter wavelengths of light (blue light), the net result is that more blue light will be reflected than red light in these dark colors. Blue wavelengths of light see greater light scatter from the titanium dioxide and do not penetrate as deeply into the medium as longer wavelengths do (red light). The resulting shorter path length for the blue portion of the incident light cause less absorption by the carbon black so that more blue light emerges and is reflected towards the observer compared to the red light. This scattering causes the blue flop which is observed when titanium dioxide is present in black color formulations.

This discussion was included here because this phenomenon can also hold true for any additive which has an index of refraction significantly different from the base polymer. In the case of the titanium dioxide example, if the blue flop was problematic in color matching, one can most likely reduce or remove the pigment from the formulation minimizing this problem. In the case where this blue flop is caused by the additive system, the effect can only be minimized by increased pigment loading. This phenomenon is also a characteristic of the base polymer as well. Most crystalline polymers will exhibit more bluish flop compared to amorphous or semi-crystalline resins due to this dependence of index of refraction on the wavelength of incident light.

The amount of scattering as you might expect depends on the magnitude of difference in refractive index between the polymer and the scattering substance. The direction of difference does not matter, only the magnitude as depicted in Figure 2. Finally, there is an optimum particle size for scattering to occur that is dependent on the index of refraction of the substance and the medium, and the wavelength of light. This optimum particle size is generally in the range of $\frac{1}{2}$ the wavelength of the incident light. Smaller or larger particle sizes will scatter less light as shown in Figure 3.

It is important to understand the mechanism of scattering because the majority of the problems in coloring polymers and blends can be related to the intrinsic whiteness or scattering of the polymer system itself. Increasing the amount of scattering in our resin system will increase the amount of diffuse reflection (white light) which is mixed with the reflected colored light generated by our pigment interactions. This mixing will dilute the color strength and the color of our object will appear

lighter and less bright to the observer. An analogy can be percolated from everyday life: coffee. Coffee without cream is said to be black (actually more like dark brown) due to light absorption by the coffee extract dispersed in water. Adding cream to the coffee increases the light scattering and the color is transformed from dark brown to light tan. And it is obvious that once the cream is added, it is impossible to color the mix with more coffee extract to achieve the original black color.

So is the case in polymers containing additive systems. As will be shown, some additive systems can impart so much light scattering to the base resin that certain colors can no longer be achieved. Or if they can be achieved, other properties may be adversely affected such as impact strength and cost. In either case, the practical color gamut or palette that is obtainable with this particular resin system is reduced. The discussion below presents the effects that the polymer and its additives can have on colorability.

Polymer Types

Transparent Resins

From the discussion above, it should be intuitive that transparent resins such as polystyrene or polycarbonate do not scatter light and therefore can achieve the most brilliant colors. Colors are generated through transmitted or reflected light without having to mix with white light from diffuse reflection since none exists from the polymer. The difficulty here is making the system opaque (no light transmission). If opacity is required, a scattering opacifier such as titanium dioxide is needed and apparent color strength will be reduced.

Translucent & Opaque Resins

Most polymers fall in the class of translucent resins. These include acetal, polyamide, polybutyleneterephthalate (PBT), polyethylene and polypropylene as examples. There are very few neat polymers that are truly opaque (this depends on thickness as well). Liquid crystal polymer (LCP) is an example of a typically opaque polymer. It is theorized that these semi-crystalline and crystalline resins will scatter some portion of incident light due to spherulitic crystal structure and the amorphous-crystalline region interfaces themselves.

The degree of translucency can be measured by calculating a contrast ratio. This number is the ratio of the L-value in color measurement obtained when backing the natural sample with a black tile divided by the L-value of the sample backed with a white tile. A completely opaque sample will have a contrast ratio of 1.00. Contrast ratio measurements are specific to the thickness of the sample and the intensity of the light source. Contrast ratios for several resins are presented in Table 1.

The data in Table 1 shows that for these crystalline resins, the contrast ratio generally increases with increased degree of crystallinity. Nylon 6,6 has the lowest contrast

ratio (less opaque) compared to liquid crystal polymer that has an extremely high crystallinity and is completely opaque. Furthermore, the two PBT samples show that the annealed sample (higher crystallinity) is also more opaque. The higher opacity indicates that more light scattering is occurring by the polymer and typically a more restricted color gamut will be achieved. Polymers with a high degree of intrinsic whiteness will exclude deep, dark colors and bright, high chroma colors from the achievable color gamut.

To illustrate this effect on colors, three single pigment colors (blue, red and yellow) were developed in three different resin systems. Blue and yellow were produced in acetal (POM), polyphenylene sulfide (PPS) and LCP. The red color was prepared in nylon 6,6, PPS and LCP. The acetal and nylon resins are translucent while the PPS and LCP are opaque at the 3.2mm sample thickness. In all three colors, the more translucent resins produced visually more brilliant, higher chroma colors than the more opaque resins with increased diffuse scattering.

Table 2 presents color data generated from these same samples. Numerically, PPS and LCP produced lighter colors (higher L* values) and/or lower chroma (C* values) compared to the acetal and nylon controls which is consistent with what is seen visually. The base resin light scattering will increase the L* value and decrease chroma in these colors. What's more, the PPS and LCP were evaluated from 2 times to 15 times the pigment loading (relative concentration) of the acetal and nylon, and this still holds true. Another indication of the increased scattering from the PPS and LCP is the relative strength data of Table 2. As shown, even at the higher relative pigment concentrations, these resins produce colors that appear only 16 to 50% as strong.

This discussion illustrates the effect light scattering of the polymer has on the resulting color. In real life, if LCP is required for a particular application, the examples in Table 2 show that deep, dark colors or bright, high chroma ones can not be achieved. If the customer is currently using these higher chroma colors in other resins such as polycarbonate, he needs to be educated that these same colors can not be achieved in LCP.

The other limiting factor in coloring a specific polymer is the stability and suitability of the colorant for a particular polymer and application. A general rule of thumb is that as the recommended processing temperature for a resin increases, the number of colorants that can withstand those temperatures decreases. Most of the colorants that drop out are organic pigments that are typically used to achieve the bright, high chroma colors or the deep, dark colors. Furthermore, polymers with harsh chemical environments like PVC, acetal or nylon limit colorants based on chemical stability. Conversely, the chemistry of the colorant can also render the polymer unstable, making it unsuitable for use as well. Finally, end use requirements such as agency compliance (FDA) or UV stability will further restrict the number of colorants that

can be used in a specific polymer. Thus the achievable color gamut for a resin system not only depends on the light scattering of the polymer but also on the types of colorants that can be utilized.

Polymer Blends

One can assume that blends of polymers will be more difficult to color than any component by themselves. Diffuse reflection can increase due to internal light reflection or scattering at phase interfaces if the polymers are at least partially immiscible or their refractive indexes are significantly different. Blends of translucent polymers are typically more opaque than either resin alone. Furthermore, colorant stability (thermal or chemical) can be adversely affected by the presence of the other polymer(s). As in the case of neat polymers, both circumstances will result in a restricted achievable color gamut for the polymer blend. An example of a prominent polymer blend is GE's Noryl® (PS/PPO) which certainly colors much differently than the polystyrene component by itself.

Blends of polymers can pose their own unique problems as well. An example is cases where colorants exhibit preferential dispersion to one of the polymer phases. The other polymer phase remains virtually uncolored. Macroscopically, this may not be a problem as the molded part appears uniformly colored. But even at this level, if wall thickness is very thin, color striations may become apparent. Other performance measures may be adversely affected as well. At the microscopic level, since all of the colorant is dispersed in one phase, impact strength and other properties may be reduced at pigment concentrations that are much lower than expected. This would primarily occur in blends where the colorant prefers the resin phase that provides the toughness to the blend.

Polymer Additives

A wide variety of additives and modifiers are incorporated into polymers and polymer blends to tailor specific properties. Unfortunately, these additives can also impact the colorability to the total resin system. Listed below are some common additives and modifiers used in polymers and a short discussion of their typical effect on colorability.

Antioxidants

In general, antioxidants will have little effect on colorability since they are typically used at low levels. At higher levels, they may increase light scattering and impact colorability depending on the polymer type. There are remote instances where antioxidants have been linked to problems with graying bright colors or "pinking" whites. But these are very polymer specific and usually result from a chemical instability within the system.

Anti-stats

These additives are designed to be present on the surface of the molded part to achieve the full anti-static benefit. Furthermore, they are typically used at higher levels than other additives such as antioxidants. Therefore, anti-stats are likely to increase light scattering making it more difficult to achieve the higher chroma colors.

Coupling Agents

Coupling agents such as silanes and titanates will increase light scattering. Both types can impact colorability if they are incorporated at high levels.

Flame Retardants

Typical flame retardant formulations will include an antimony compound, a bromine compound, and possibly a drip suppressant. All three additives will significantly increase light scattering and reduce the color gamut of the resin. Table 3 presents color data to show this effect. Eight flame retardant polyester colors are listed with lightness, chroma and strength differences calculated versus the same colors in neat polyester resin. All colors are lighter (positive DL*) and duller with lower chroma (negative DC*) with the presence of the flame retardant system. Relative color strength data also shows that the colors are weaker and less intense. It would be difficult if not impossible to exactly match the neat polymer color in the flame retardant system due to the light scattering of the additives.

Foaming Agents

The author has little experience with foamed resins. However, one would speculate based on all of the above information that foaming would increase light scattering since the molded parts would contain a complex cell structure with all of its polymer/gas interfaces.

Heat Stabilizers

Antioxidants can be referred to as heat stabilizers and were previously discussed. Other heat stabilizers are metal complexes used in PVC and nylon. The largest impact on colorability is with the metal complexes used to increase the continuous use temperature rating in nylon. In that resin, these metal complexes can significantly reduce colorability due to discoloration via reaction with the colorant, or by thermal degradation. Light colors in heat stabilized nylon are virtually impossible to control since a slight change in residence time or temperature will significantly drive the color to tan or brown. The presence of oxygen will accelerate this. Darker colors are less affected and are preferred in heat stabilized nylon.

Impact Modifiers

This class of additives covers a broad range from butadiene to acrylic polymers. Since these additives are polymeric in nature, diffuse reflection will occur at the polymer/modifier interfaces similar to polymer blends.

Again, this will result in colors that appear lighter and duller. Table 5 contains three examples of impact modified colors compared to the neat resin without modifier. As expected, the impact modified colors are lighter and have lower chroma. In practice, ABS or HIPS would have a more restricted color gamut compared to their transparent SAN and PS base polymers.

Lubricants/Mold Releases

Like anti-stats, lubricants and mold releases are designed to reside on the molded part surface. Therefore, light scattering can be increased depending on the chemistry and concentration of additive. Generally this effect is not a problem unless these additives are used at high levels, or they have significantly different refractive indexes from the base polymer. Table 4 shows color difference data for two colors containing a high level of lubricant versus a polymer with no lubricant. Increased light scattering is evident by the lighter color (positive DL*) and lower relative color strength.

Reinforcing Agents

Reinforcing agents are typically either a mineral such as talc and calcium carbonate, or fiberglass. As expected, mineral types used at their high levels can scatter a large portion of the incident light depending on the refractive index and particle size. In mineral filled resins, it is usually impossible to achieve deep, dark colors such as chocolate brown or forest green. Bright colors are also made duller. Because a high amount of mineral is generally used, bright white colors such as appliance white can also be difficult to achieve.

Fiberglass poses a different problem in that colors are typically darker and more dingy looking in glass reinforced resins versus their unfilled counterparts. Table 6 lists color difference data for several 30% glass reinforced PBT colors versus the same color in unfilled PBT. The darker, dingier look is evident by the negative lightness and chroma difference values. Brighter, high chroma colors in glass reinforced resins either require significantly more colorant to achieve (at higher cost) or can not be exactly matched due to the resin. Overcoming the darkness makes bright white colors difficult to achieve as well. Contributing factors to the dark, dingy appearance are most likely the glass sizing agent and the elevated processing temperatures for glass reinforced resin versus the unfilled product.

Fiberglass adds another problem to coloring: mechanical property retention. A number of widely used colorants will abrade glass fiber length or can affect fiber wetting significantly reducing properties. For example, in 30% glass reinforced PBT, certain colorants can reduce tensile strength up to 20% and notched izod impact by as much as 30%. And this reduction occurs using colorant concentrations that would be termed typical and not excessive. Mechanical property retention may further limit the types and numbers of colorants that can be used in the

glass reinforced resin, further limiting its achievable color gamut.

UV Stabilizers

A large number of colored polymers and polymer blends are used in applications where UV stability is important. First and foremost, many common colorants do not possess satisfactory lightfastness to be used in UV applications. Therefore, the color gamut can be reduced due to limited availability of colorants with acceptable lightfastness in certain polymer systems. UV stabilizers themselves can also impact colorability. Many impart a yellowish tint to the polymer that must be overcome. Also, some do increase light scattering making the more popular automotive maroon and dark blue colors difficult to achieve.

Conclusion

References

1. F. W. Billmeyer, Jr. and M. Saltzman, Principles of Color Technology, 2nd ed., John Wiley & Sons, New York, p. 12 (1981)
2. R. A. Charvat, Coloring of Plastics Fundamentals, 2nd ed., John Wiley & Sons, New Jersey, p. 341 (2004)

Hopefully, the discussion and examples presented above have clearly shown that color should be engineered along with other desired thermal and mechanical properties. That way, either the desired color can be formulated to minimize property loss, or the closest achievable color can be developed. And understanding the color limitations early on can help steer customers to those colors that can be achieved, which may be different from those actually desired.

Most of the discussion has been centered around just the neat polymer or the polymer plus a modifier or additive. Coloring issues further escalate when polymer blends are used or when multiple additives are incorporated. Would it be difficult, and would the color gamut be somewhat restricted, if one was to color an impact modified, flame retardant, glass reinforced PBT/polycarbonate alloy? The answer now better be a resounding YES!

Figures

Figure 1
Refractive Index Diagram

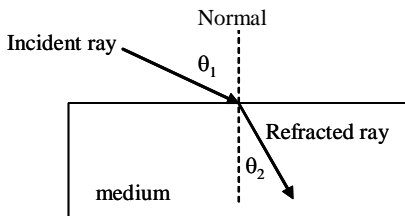


Figure 2
Scattering as a Function of Refractive Index Difference

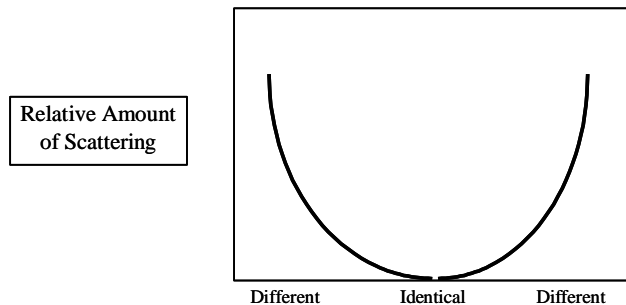
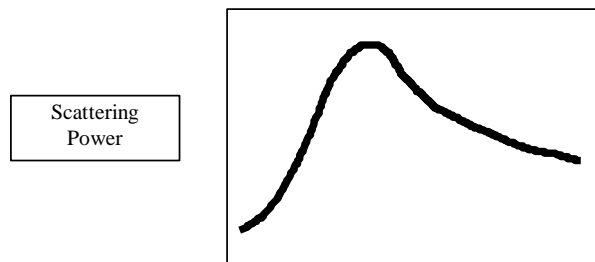


Figure 3
Scattering as a Function of Constituent Particle Size



Data Tables

Color data presented in the following tables have been calculated under illuminant “D-65”, 10° observer, specular included, expressed in CIELab units, unless otherwise noted.

Table 1
Contrast Ratios of Selected Resins

Resin	L-value† White	L-value Black	Contrast Ratio @ 3.2mm
Nylon 6,6	85.65	66.75	0.78
Acetal	93.01	82.05	0.88
PBT	92.70	87.14	0.94
PBT (annealed)	92.80	90.94	0.98
LCP	84.10	84.10	1.00

† Specular excluded, expressed in HunterLab units

Table 2
Relative Color Strength in Various Resins

Color	Resin	Relative Concentration	L*	C*	Relative Strength
Blue	POM	X	37.05	55.01	
	PPS	3X	47.78	34.34	42 %
	LCP	3X	61.60	27.93	16 %
	LCP	6X	56.14	35.09	26 %
Red	Nylon 6,6	X	35.91	41.61	
	PPS	3X	44.43	33.67	48 %
	LCP	3X	56.87	34.13	23 %
Yellow	POM	X	77.52	77.94	
	PPS	2X	69.35	52.45	50 %
	LCP	15X	78.13	51.03	31 %

Table 3
Effect of Flame Retardants on Colorability
(FR Resin Versus Neat Polymer)

Color	DL*	DC*	Relative Strength
Bright Yellow	2.3	- 3.5	56 %

Bright Red	4.9	- 7.1	53 %
Medium Tan	7.0	- 2.4	57 %
Bright Orange	4.0	- 1.5	74 %
Royal Blue	6.3	- 3.2	78 %
Dark Green	9.3	n/a	52 %
Medium Gray	5.0	- 0.5	n/a
Black	3.4	- 0.9	72 %

Table 4
Effect of Lubricant on Colorability

Color	DL*	Relative Strength
Bright Red	1.6	85 %
Dark Blue	2.7	80 %

Table 5
Effect of Impact Modifier on Colorability

Color	DL*	DC*
Gray	4.5	- 1.8
Bright Red	2.8	- 2.4
Bright Yellow	3.6	- 4.0

Table 6
Effect of Fiberglass on Colorability

Color	DL*	DC*
Gray	- 1.8	- 0.2
Dark Blue	- 1.5	- 0.7
Bright Yellow	- 5.9	- 8.2
Dark Green	- 3.5	- 2.9
Bright Red	- 1.7	- 0.6