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Authors: Mark S.Harber & John J.Young
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Technical Paper

Carbon Black: Theory and Uses in Thermoset Composite Applications

Abstract

Carbon black is an intense black powder or bead that functions as an indispensable pigmenting and property-modifying agent in a wide range of composite products. Certain unique product characteristics make carbon black a very valuable part of many thermoset composite formulations. These characteristics include the ability to provide polymer protection by absorbing damaging UV energy and converting it into thermal energy, it's ability to enhance electrical conductivity, and it's intensity when used to pigment composite parts. This paper will analyze and explain the different grades of carbon blacks that are currently available for thermoset composite applications.

Introduction

Carbon black as a thermoset composite colorant. The general idea of coloring thermoset composites black or perhaps a dark gray seems simple and straightforward. One could simply add a dispersion of carbon black or a carbon black powder to the composite formulation. While in theory this sounds very uncomplicated, in practice it can be technically challenging. Carbon black pigments are used not only as a colorant, they are very efficient at absorbing light across the visible spectrum and the ultraviolet spectrum. Carbon black is also popular in a myriad of other applications such as automobile coatings, tires, laser and ink jet printers, and the coloration of many types of plastics. There are a few terms used with carbon black pigments that we will need to define:

Tinting Strength. The tinting strength of a carbon black pigment measures the ability of the pigment to overpower other fillers, extenders, and additives that may be used. The tinting strength of carbon black can be a relative term. For this paper, we will choose the weakest carbon black and assign it the value of 100 percent.

Undertone. The various different shades of black or gray color that occur when incorporating carbon black with other light colored pigments or fillers. This term can also apply to certain low shrink or low profile additives, since they can act as a whitening agent (very similar to titanium dioxide or zinc sulfide pigments) in certain composite applications.

The CIE (Commission Internationale de l'Eclairage, 1976) L*a*b* coordinate system. This three-axis system is used by various industries to communicate color and/or color differences. A simple representation of this system comprised of the three axes **L***, **a***, and **b***, are shown in Figure 1.

- **L***: (Light-Dark) Lower L* values would be attributed to a "jetter" or "blacker" carbon black.
- **a*** : (Red-Green) Higher values for a* indicate that the color is more red; lower values for a* indicates that the color is more green.
- **b*** : (Yellow-Blue) Higher values for b* indicate that the color is more yellow, lower values for b* indicates that the color is more blue.

The Significance of L*, a*, and b* values. When measuring the blackness or the jetness, a lower L* value would indicate that a part should visually appear darker if compared to another part with a corresponding higher L* value. This is usually straightforward and easy to obtain visual agreement. The b* measurement is also important. There can be different undertones associated with carbon black, even if the L* values are nearly identical. How can that be? That is where the concept of undertone becomes important. If one composite part has a lower b* value when compared to another, it will appear to be more blue, even if the L* values are identical. The a* value can also influence the overall appearance.

Conductive carbon black. Thermoset composites, including many types of unsaturated polyester, epoxy, and vinyl ester resins will normally behave as insulators. General furnace process carbon black pigments that are used as colorants for composite applications are typically resistive in nature; thus they are not suitable for conductive applications. Special types of carbon black must be used to color the composite part and also make the formulation conductive. The methods of incorporation and effectiveness of dispersion are important in developing good conductivity properties in thermoset applications. To make a composite panel conductive and to ensure that the surface coating application is enhanced, an optimum percentage level of conductive carbon black and the right combination of raw materials are required.

Electrostatic painting is gaining industry interest because of the stringent regulations governing the emissions of VOC's (volatile organic compounds), potential increases in quality and production, and possible decreases in total painting costs. This would be attributed from the reduction of overspray material that normally would not have been deposited successfully on the part. Electrostatic painting is accomplished by negatively charging atomized paint particles so that they are attracted to the grounded conductive composite panel. An electrode is located at the tip of the electrostatic spray gun. The paint is finely atomized as it moves past the electrode, and during that process the atomized particles become ionized and negatively charged. An electrostatic field is created between the charging electrode and the grounded composite panel. As a result of this electrostatic attraction, spray that would normally be wasted to the surroundings should in practice end up on the back and sides of the composite part that the coating is being applied to.

Conductive carbon blacks are a unique category of carbon black. Properties that are important to conductive carbon blacks are:

- Smaller particle size which equates to large surface area per unit weight
- Higher structures which tends toward increased conductivity
- Surface chemistries that have very low amounts of oxygen on the surface of the carbon

Unfortunately these properties are not ideal for producing dispersions with high conductive carbon black levels. Most of the wetting, dispersion, and viscosity properties that we would like to see in a regular grade of carbon black colorant are more or less the opposite case for conductive carbon blacks. Polymer family can have a great influence on conductivity, thus the resin chemistry and the interaction of low shrink/low profile additives must be considered. The required electrical resistance range for the specific application must be determined and defined during the early product design stages. Formulation, processing, and storage conditions must be studied and closely followed.

Objective

Polymer Type and Selection Study (SC and LC)

The wetting and dispersing properties of carbon black can vary based on the types and grades of carbon blacks used as well as the properties of polymers that are employed as carrier resins (also known as grinding vehicles). Changes to the polymer chemistry can have a potential effect on the final product dispersion viscosity, so it was decided to make some adjustments during the resin synthesis stages. The overall goal was to learn what type(s) of polymer chemistries would accept higher percentage by weight loading of carbon black without causing any detrimental change in other physical or mechanical properties.

Tinting Strength and Undertone Studies (TSU)

The tinting strength and the color undertone of a carbon black can change when the structure and particle size of the carbon black is changed. Titanium dioxide is one of the whitest and most intense pigments available on a commercial basis. It was decided to evaluate the tinting strength and dispersion undertone with titanium dioxide since it could potentially provide some valuable information about the performance of a particular grade of carbon black. It was determined that the study of the L* (light-dark) values, the b* values (blue-yellow), and the a* values would be very beneficial, as well as measuring the relative tinting strength of each dispersion.

High Carbon /Low Viscosity Technology (HCLV)

There is general interest from many composite fabricators to utilize a carbon black dispersion that is very high in carbon black concentration, and also can be easily pouredor pumped for viscosity-sensitive requirements. Until recently, this would have been considered a very difficult or otherwise cost-prohibitive proposition.

Based on information gathered during the initial polymer type and selection studies, it was decided to continue refining these processes so that significantly strong versions of carbon black dispersions could be developed that could easily poured, pumped, or metered in large-scale production environments.

Conductive Carbon Study (CCA)

Conductive carbon black is a specific manufacturing segment of carbon black technology that is gaining the interest of automotive manufacturers. As covered in the introductory section, the painting of thermoset composite parts by an electrostatic process is already under intense investigation by some automotive manufacturers in the United States and Europe. The specific area of interest is modifying composite part formulations so that they are conductive. This requires the incorporation of conductive carbon black pigments and/or other specialty additives. A study was implemented to monitor a Class A sheet molding compound (SMC) that was designed for a conductive application. It was decided that the minimum stability requirement for would be a minimum of four weeks (28 days). The study would take separate measurements over a specific elapsed time.

Experimental

Polymer Type and Selection Study (SC and LC)

Ten separate formulations were made. All ten formulations were high-speed dispersed and also processed on a three roll mill. (SC) standard viscosity carrier resin experiments SC-1 through SC-5 were 20.0, 25.0, 35.0, and 37.5 percent by weight respectively of a widely used utility-grade carbon black. (LC) lower viscosity carrier experiments LC-1 through LC-5 were prepared in the same manner, using carbon black at 20.0, 25.0, 35.0, and 37.5 percent by weight.

All of the experiments used the same grade and production lot of carbon black. The only variable was the substitution of a different synthesized polymer. The LC version had the same chemical components that comprised the standard carrier SC; however, the molar charge and the polymer synthesis techniques were varied to produce a resin that would theoretically accept a higher carbon black charge weight. Viscosity values were measured with Brookfield HBT-DVII+ and RVF viscometers.

Tinting Strength / Undertone Study (TSU)

Five separate formulations were made. Five different grades of carbon black pigment were evaluated. The carrier resin was the same for all five experiments. The carbon black pigments were selected based on a range of different particle sizes and structures. The carbon black loading levels were fixed at 20.0 percent by weight, with the balance of the formulation being made with standard viscosity (SC) carrier resin.
Each carbon black dispersion was evaluated using a mixture of 20.0 percent by weight of the carbon black dispersion and 80.0 percent by weight of a titanium dioxide white pigment paste. The titanium dioxide paste was a dispersion made with 70.0 percent by weight rutile titanium dioxide and 30.0 percent by weight standard viscosity (SC) carrier resin. The mixtures were introduced into a thermosetting polyester resin at 4.0 percent by weight and the cured castings were prepared. The CIE L*a*b* values were tabulated for discussion. Tinting strength percent differences were reported with the lowest strength (lowest L* value) dispersion being assigned a reference value of 100 percent.

High Carbon /Low Viscosity Technology Study (HCLV)

Four new high strength/low viscosity (HCLV) formulations were investigated. Optimized polymer packages were synthesized. A carbon black with improved wetting and dispersion characteristics was used in conjunction with a new polymer package. This unique grade of carbon black was used to make all of the HCLV dispersions.

The four formulations were high-speed dispersed and also processed on a three roll mill. HCLV-1 was made at 35.0, HCLV-2 at 40.0, HCLV-3 at 45.0, and HCLV-4 at 50.0 percent by weight carbon black. Viscosity values were measured at room temperature (25C) with a Brookfield RVF viscometer.

Conductive Carbon Study (CCA)

A conductive SMC formulation was compounded to research automotive Class-A application. The target conductivity value was 0.5 to 2.0 Meg Ohm surface resistance when measured with a ITW Ransburg model 76634-00 meter. Sheet molding compound was manufactured and molded at 2 day, 13 day, and 28 day intervals, to measure and study any possible changes in conductivity or molding properties over time.

Results and Discussion

Polymer Type and Selection Study (SC and LC)

Figure 2 illustrates the difference of dispersion viscosity when the carbon black type is fixed and the polymer types are varied. Throughout the range of carbon concentrations tested, carrier LC resulted in improving the product viscosity. At 37.5 percent by weight carbon the standard carrier SC had a viscosity of 1,460,000 cp., while the improved carrier LC had a viscosity of 922,000 cp. The overall product viscosity was reduced 51,200 cp. at 20.0 percent carbon, 71,000 cp. at 25.0 percent carbon, 266,000 cp. at 35.0 percent, and 538,000 cp. at 37.5 percent carbon. The promising initial results of these studies led to the refinement and design of the high carbon /low viscosity (HCLV) products.

Tinting Strength / Undertone Study (TSU)

The results of the tinting strength and undertone study (TSU) are listed in Table 1. The results followed a general trend that is recognized in other rubber, coatings, and plastics industries. The larger particle size carbon blacks measured in nanometers (1 nm = 10^{-9} meter) were higher in L* value (thus weaker) than the smaller particle size blacks. The ranges of tinting strength varied from 100 to 159 percent, depending on the grade being evaluated.

The larger particle size carbon blacks were also more blue in undertone (b* values lower) than the smaller particle size carbon blacks. The larger particle size carbon blacks tended to be not as red in undertone (a* values lower) than the smaller particle size carbon blacks.

It is important to point out that while the trend is generally observed, there are cases where it can differ. This is related to a combination of carbon black properties such as particle size, structure, and surface treatment.

High Carbon /Low Viscosity Technology Study (HCLV)

The results of the HCLV experiments indicated a significant improvement in product viscosity, even when the carbon black loading was increased to 50.0 percent by weight. For example, a viscosity of 2,400 cp. was attainable at a 35.0 percent by weight carbon black level, while the best counterpart product (35.0 percent by weight, LV) from the previous round of experiments measured 532,000 cp.

Figure 3 illustrates the differences of the finished dispersion viscosity when polymers are synthesized to specifically match the wetting properties of a carbon black pigment.

Conductive Carbon Study (CCA)

The 12"x12" sheet molding compound (SMC) panels exhibited very good conductivity in the k-Ohm (10^3) range. The panel was divided into nine square regions that were 4" x 4" in size. The conductivity measurements were taken in the center of each region. The initial charge pattern and the flow could explain some of the differences of the conductivity values. It was discovered that a slight change in pressure during a conductivity measurement could result in some hysterysis, especially in the lower regions of the conductivity scale. Based upon this information, the meter was allowed to rest perpendicular to the surface of the panel while being held in place with a nonconductive acrylic support, with no additional pressure applied. The conductivity versus aging indicates that within a 28 day molding window, no appreciable loss in conductivity was observed. Table 2 shows the results of the conductivity versus the elapsed storage time (in days) of the sheet molding compound.

Conclusion

Generic colorant guidelines. For general-purpose applications, larger particle size, blue undertone carbon black pigments have generally been preferred by the thermoset market segment and can often be the most economical choice. In general terms, larger particle size, low structure grades can be introduced at higher percentages in thermoset resin polymers. The larger particle size carbon black tended to be weaker in tinting strength, at equal loading level. A smaller particle size carbon black could be substituted (possible at a lower percentage by weight) to maintain the same L* value, thus it would be a match for shades of lightness or darkness. However, one would have to consider the additional effect of the b* value, and also the a* value. The smaller particle size carbon blacks tend to be browner and more distinct, while the large particle size carbon blacks tend to be bluer and somewhat less distinct. There are other additional factors to consider. Fillers, extenders, glass fibers, and low shrink/ low profile additives can alter the undertone.

Polymer Selection. Specifically designed polyester resin polymers can reduce the viscosity of carbon black dispersions. The effects of the polymer as related to the dispersion viscosity become very noticeable at levels above 20.0 percent by weight of carbon black. The loading of carbon black dispersions could also be increased while maintaining the viscosity profile of the original product.

High Carbon/Low Viscosity (HCLV). Optimization and polymer synthesis, in combination with special carbon black surface treatments can result in dispersions that are low in viscosity and high in carbon black content. The refinement of synthesized carrier polymers and careful of the carbon black grade in used in conjunction with specifically designed polymers has a very positive effect on lowering the dispersion viscosity. Specific resin selection of carbon black types yields a new range of manufacturing flexibility for the composite fabricator. Manufacturers of composite parts can have the ability to pour, pump, or even meter high concentration carbon black liquids with equipment using mass flow or loss-in-weight controls.

Conductive carbon black. The automotive market sector continues to generate interest in conductive Sheet Molding Compounds (SMC). There are new challenges that come along with conductive polymers. Conductive carbon black is not normally easy to incorporate from a percentage carbon loading and viscosity standpoint. A great deal of research is being done to optimize the amount of conductive carbon black in thermoset polymers, and to design polymers that will result in lower viscosity products without physical or mechanical property penalties.

It is important to study the complex relationships of filler types, amounts, and filler combinations. Any changes in the dispersion process, additives, fillers, initiators, chemical thickeners, and resin chemistry can affect conductivity of finished part. Storage requirements are also important, and studies must be made to ensure that conductivity can be maintained for at least three to four weeks after the sheet molding compound is made.

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AUTHORS

Mark S. Harber
Mark S. Harber joined AOC (The Alpha Corporation) in 1982, and he has served as Technical Service Manager for AOC's Chroma-Tek colorants since 1986. He received a B.S. degree in Mechanical Engineering from the University of Memphis, Memphis, Tennessee.

John J. Young
John J. Young joined AOC (Owens Corning) in 1985, and is the Closed Mold Product Leader for the Technical Services Organization (TSO) in Valparaiso, Indiana. John received his B.S. in Chemistry and M.S. in Polymer Science from the University of Akron, Akron, Ohio.

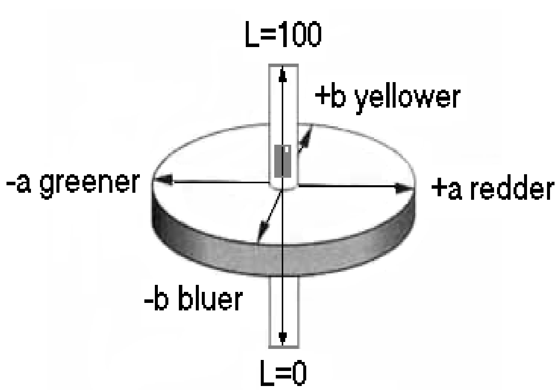

Figure 1. Representation of the L*, a*, and b* axes.

Figure 2. Polymer Type and Selection Study.

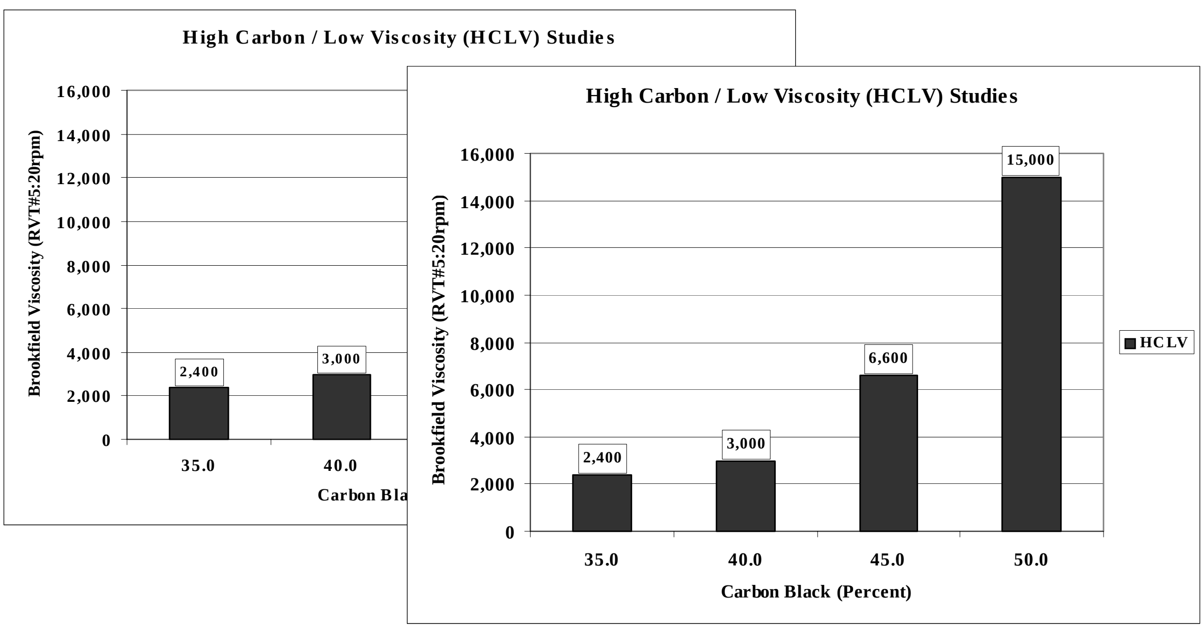

Figure 3. High Carbon / Low Viscosity (HCLV) Studies

Particle Size (nm)	L*	a*	b*	Strength
21	42.32	-0.74	-2.78	159
24	42.56	-0.74	-2.73	157
34	46.26	-1.02	-3.97	123
53	47.98	-1.17	-4.38	110
101	49.38	-1.30	-4.75	100

Table 1. Tinting strength and undertone (TSU) studies.

	Ejector Side			Opposite Side		
2 Day	300	410	270	350	460	360
	370	490	440	390	570	330
	460	320	390	310	310	250
13 Day	360	500	410	400	420	370
	420	400	420	370	540	590
	500	360	330	380	420	290
28 Day	330	360	420	399	400	330
	350	410	440	440	350	580
	370	400	320	320	390	290

Point for comparison when panel is reversed

Table 2. Conductivity (k-Ohm) versus aging in 12"x12" panels (CCA).