Designing Pigments for Optimal Performance in Chemical Toners

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Abstract

Carbon black has historically been used in electrophotographic toners as a black pigment. Its properties influence some of the key performance attributes of the toner, including the printed image density and the toner's electrical characteristics. In the last decade demand for higher resolution and lower cost printing has driven significant improvements in toner performance. These changes have shifted the production of new toners from the conventional pulverization process to more complex chemical processes. In these new processes, carbon black and the other pigments are typically first dispersed into a liquid matrix (aqueous or organic solvent or monomer) and are then incorporated into the toner particle either by chemical assembly processes, such as emulsion aggregation, or direct polymerization. Throughout the various process steps the carbon black needs to remain dispersed in the matrix to optimize the performance.

Cabot has developed surface modification technology that allows the design of the carbon black surface chemistry to match the properties of its surrounding matrix. In this presentation we will explore the sensitivity of the carbon black dispersion quality to changes in the polymer properties. We will also demonstrate how careful control of the surface chemistry can enhance the dispersion of the carbon black.

Introduction

Toner particles have always been pigmented polymer composites that contain enough pigment (black or color) to yield the appropriate image characteristics after transfer and fusion to the paper. Carbon black has been the dominant black pigment and its morphology and properties influence both the color properties of the toner and its electrical charging characteristics [1]. Both of these properties depend on the quality of the dispersion of the carbon black in the composites. Historically toner particles have been prepared by compounding the pigments into the polymers followed by a grinding/classification process. As the demand has increased for lower total cost of ownership and higher resolution printing, the toner industry has shifted its manufacturing processes to chemical processes, as illustrated in Figure 1 below.

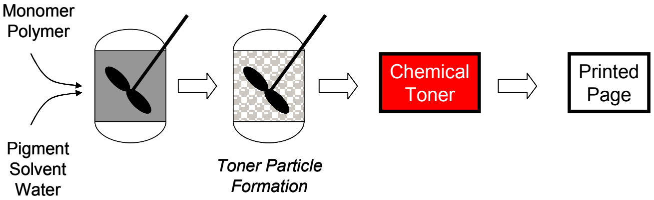

***Figure 1**. Steps in Chemical Toner Preparation and Use*

In these processes the pigments are dispersed first in a liquid phase (water, solvent, or monomer depending on the process), and are then incorporated into the polymer either through an agglomeration process or through polymerization around the pigments. In both of these cases, there is no further dispersion of the pigment into the toner polymer. This creates a challenge for both the toner formulators and the pigment suppliers, as the pigments need to remain dispersed in phases that are chemically very different without the application of any mechanical energy.

In this paper we describe some advances in the design of modified carbon black particles that enables the design of the surface energy of the pigments to allow for customization of their compatibility with the surrounding matrix. Applications that illustrate the effects of different surface chemistries on polymer compatibility will be described.

Carbon Black and Surface Modification

Carbon black is manufactured by the thermal decomposition of hydrocarbons and consists of elemental carbon in the form of nearly spherical primary particles of colloidal size, fused into aggregates. These aggregates form larger agglomerates during the carbon black densification. Through control of the manufacturing conditions, it is possible to independently control the *size* of the primary particles, and the *number* of primary particles fused into the aggregates, manifested indirectly in the size of the aggregates. A transmission electron microscopy (TEM) image of a typical toner carbon black grade is shown in Figure 2. The physical properties of carbon black that are indirect measures of these two fundamental properties are its surface area (m^2/g) and its oil absorption number (OAN – ml/100g). Existing carbon black grades cover a broad range of morphologies to provide aggregates having performance targeted to the end use. The carbon black grades used in toner applications have a balanced primary particle size and structure to allow for good color properties, ease of dispersion, while providing controlled electrical resistivity to the toner to allow for the design of its charging characteristics.

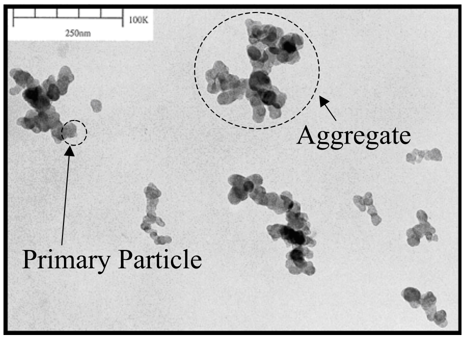

***Figure 2.** Morphology of carbon black particles.*

Cabot has developed proprietary chemical modification technologies that can be used to alter the surface chemistry of the pigment. One type of chemical modification technology utilizes diazonium salt intermediates to attach a variety of functional groups to carbon black [2]. The reaction chemistry is summarized in Figure 3. The treating agent contains a functional group R, which can be varied according to the application requirements.

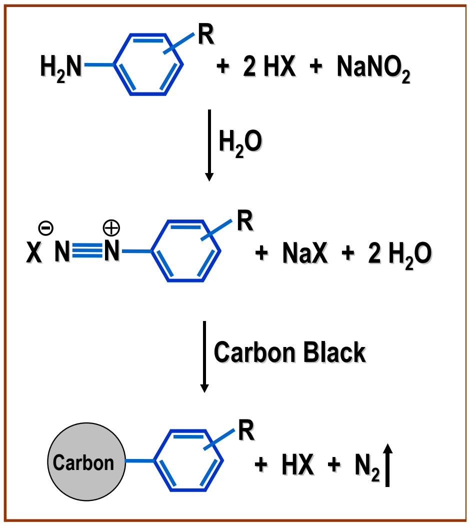

Figure 3. *Chemistry of Carbon Black Surface Modification.*

Pigment treatment technologies, such as the diazonium treatment technology can allow not only the control of the surface chemistry of the modified carbon blacks, but also the control of the extent of modification. The surface coverage is optimized by varying the stoichiometry per unit surface area of the carbon black; typically the coverage reaches a maximum at levels corresponding to the theoretical coverage with a monolayer of functional groups, which is a strong function of their size and shape. This surface modification technology enables the control of the surface energy of the modified carbon black (MCB) pigment. For this study we have prepared carbon blacks that have distinctly different surface groups at similar coverage levels (see Table 1) and studied their compatibility with a variety of systems.

Table 1. *Range of modified carbon blacks prepared for testing with toner polymers (patent pending).*

Carbon	**Functionality**
Base Carbon	None
MCB – 1	Aromatic
MCB – 2	Alkyl-aromatic
MCB – 3	Alkyl ester of aromatic
MCB – 4	Oxidized
MCB – 5	Strong acid

Characterization of Carbon Black Surface Energetics

The surface energy of the modified carbon blacks described in Table 1 was characterized using water adsorption measurements. These measurements are very sensitive to the type of functional groups that are on the carbon black surface and allowed us to rank the hydrophilicity of the materials relative to the starting carbon. The results are summarized in Figure 4 below. As expected the aromatic and alkyl-substituted aromatic carbons (MCB – 1, MCB – 2) are slightly more hydrophobic than the starting material, while the attachment of oxygen containing functional groups increase the hydrophilicity of the surface. Alkyl ester groups (MCB - 3) are still quite hydrophobic compared to carbons functionalized with strong acid groups (MCB – 5). As expected an oxidized version of the base carbon black (MCB – 4) appears to have more moderate hydrophilicity.

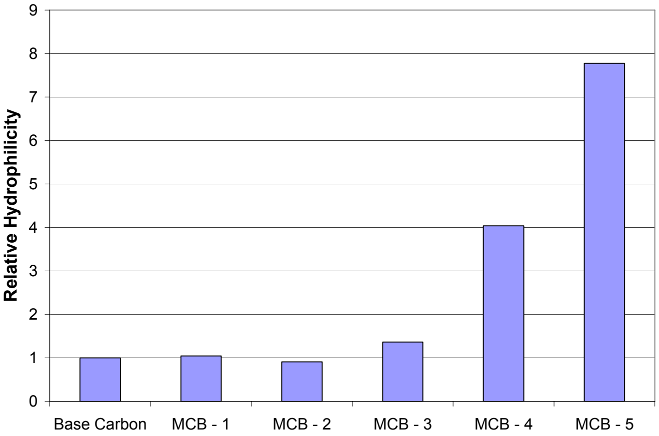

Figure 4*. Hydrophilicity of modified carbon blacks relative to base material.*

Preparation of Toner Polymer Composites

The characterization of the compatibility of the modified carbon blacks with the polymers can be evaluated without preparing chemical toner, as it is not dictated by the kinetics of the toner particle assembly processes but rather by the inherent thermodynamics of the particle-polymer interactions. In order to probe the compatibility of the various modified carbon blacks with polymers we have prepared composites using traditional melt mixing techniques. For this study we have used three typical toner polymers (two styrene acrylics and one polyester) to illustrate the effects of surface chemistry on polymer compatibility.

The samples are prepared in three stages. First the Brabender mixer head is preheated to the desired temperature, the mixer is turned on, and a premix of carbon black and polymer is poured into the mixing chamber slowly. The materials are typically mixed for 30 minutes, and then the mixer is stopped, left to cool down and the composite is removed from the mixer. Then the material is pressed at 177 ^{o}C and 17 MPa for 5 minutes between Mylar sheets that are placed between stainless steel plates. 0.8 mg pieces of film are chipped off and placed between glass slides that are clamped in place with binder clips. Two slides are prepared: one is placed in a 200 ^{o}C oven for 5 minutes, and one which is placed in the same oven overnight. Both slides are inspected visually and using optical microscopy. These techniques reveal a lot of information about the dispersion quality of the modified carbon blacks in the different polymers and allow us to look for the effects of surface chemistry.

Characterization of Dispersion Quality

Styrene acrylic resins:

We compare results obtained with typical toner industry styrene acrylic polymers that differ primarily in their acid number (AN): one is a neutral resin with a low AN, whereas the other is an acidic resin with a medium AN. The optical microscopy pictures of the various composites prepared at 2.5 wt% carbon black loading before and after the overnight heating are shown in Figure 5.

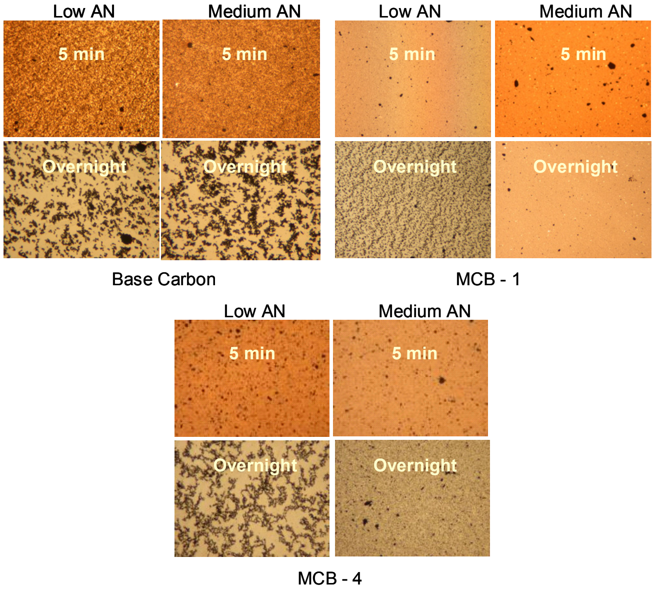

***Figure 5**. Optical microscopy images of 2.5% carbon black/styrene acrylic films at 100x magnification.*

All materials form moderately good dispersions in the polymer, as can be seen in the *5 min* images. The Brabender mixer creates enough shear force in the compound to disperse the pigment and because the samples subsequently spent 5 minutes at an elevated temperature the system state is frozen soon after the shear force is applied. In fact, most pulverized toners would show dispersion quality levels even better than what we can see in the *5 min* images. This is due in large part to the higher shear forces developed in commercial compounding operations where the pigment loading is much higher (~7-10 wt%) than the pigment loading for this experiment (2.5 wt%).

When we examine the *overnight* images, we can see that in some cases, the pigment has flocculated in the polymers and formed extensive networks. The base carbon appears to be incompatible with both resins that were tested. This is evident from the pictures of the slides that were left overnight at 200 °C. On the other hand, the oxidized MCB – 4 shows good compatibility with the medium AN styrene/acrylic resin and poor dispersibility in the low AN resin. MCB - 1 shows good compatibility with both polymers under all conditions. This is likely due to the specific aromatic functionality that has been attached to the carbon black, which has affinity to the styrene groups in the resin.

Polyester resins:

Reichhold Fine Tone T-382ES-HMW is a bisphenol-A derived polyester with an acid number of 18 and was used as a model polyester resin in this study. Materials were blended at 5 wt% loading. We observed the optical microscopy slides once they were prepared, and realized that there was again a huge difference in the dispersion of the various modified carbons. A picture of the six slides is shown in Figure 6. The MCB - 1,2, and 3 slides are clearly darker than the base carbon and the MCB – 4 and 5. This is an indication that these materials have dispersed much better into the polyester resin, and thus can yield better color. The base carbon and the two more hydrophilic carbons appear to have much poorer dispersibility. We believe that this is attributable to the surface chemistry on the MCBs. MCBs 1 and 2 are hydrophobic, and have affinity for the aromatic component of the polyester, whereas MCB – 3 has an ester functionality, which is also compatible with the resin.

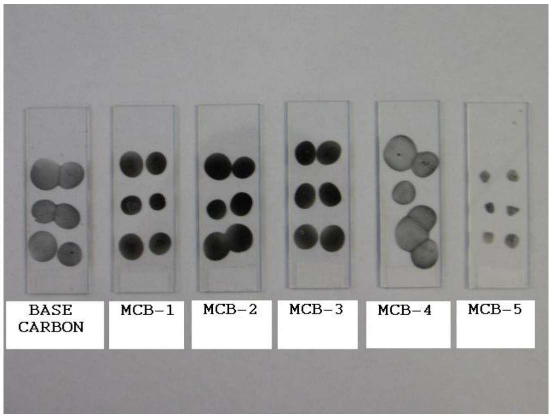

***Figure 6.** Slides containing buttons of 5 wt% composites of MCBs in polyester resins.*

Conclusions

In this manuscript we have shared some of our findings on how changing the surface chemistry of carbon black can have a huge impact on its compatibility with the two main types of toner polymers. Good compatibility is the first prerequisite to forming and maintaining an excellent dispersion of the carbon black in the toner that will help to maximize the toner performance.

References

[1] Jean-Baptiste Donnet, Roop Chand Bansal, Meng-Jiao Wang, “Carbon Black. Second Edition”, Marcel Dekker, (1993).
[2] See for example US Patents 5,554,739 and 5,922,118.
[3] Reichhold website (www.reichhold.com)

Author Biographies

Angelos Kyrlidis received his Diploma in Chemical Engineering from the National Technical University of Athens, Greece (1987) and his PhD in Chemical Engineering from the Massachusetts Institute of Technology (1993). He worked at the Lawrence Berkeley Laboratory and Molten Metal Technology before joining Cabot Corporation in 1998. His work has focused on the development of new surface modified pigments for a variety of applications, including toners.

Anne Shim received her Masters in Engineering from the Technical University of Denmark, Lyngby (1997) and her PhD in Polymer Science from the University of Akron (1998). She worked at Dow Corning before joining Cabot Corporation in 2006. Her work has focused on the development of modified pigment dispersions in organic solvents.