

New Methods of Carbon Black Surface Modification

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Abstract

The modification of the surface of carbon black is an important tool to adjust its material properties for different applications. Besides the well-known oxidation processes some new routes of surface modification were established in the last couple of years. The main feature of these new technologies is the formation of a chemical bond between the carbon black and the modification agent.

This paper is intended to give an overview on new modification methods which lead to a wide range of different types of carbon black. These technologies, e.g. polymer grafting, reactions with diazonium salts and radical initiators, open up the opportunity to influence the material surface, giving rise to changes from intense hydrophilic to strong hydrophobic.

An effective tool to attach modification agents on the carbon black surface is the well-known chemistry by Otto Diels and Kurt Alder. First published 75 years ago the so-called Diels-Alder reaction became a key also to new types of carbon blacks. With this reaction type it is possible to create products with variable polarities between hydrophilic and hydrophobic in order to tailor solutions for applications with special requirements. For this development the availability of new characterization methods like special DRIFTS and NMR analyses played an important role.

The main targets for the commercial use of these new products are NIP (non-impact printing) applications like ink jet and electrophotography, along with coating applications.

1. Introduction

Carbon black has been considered to be more or less as a chemically inert pigment. Used already by the ancient Chinese 2000 B.C.,¹ the first patent application dealing with oxidative after-treatment stems from 1918.²

The oxidation of carbon black is the most common treatment method practised. The resulting products are in use especially as pigments in coatings, high-quality printing inks, and ink jet inks. There are different established oxidation processes making use of oxidation agents like nitric acid,³ ozone⁴ or hypochlorites.⁵

In general the oxidation generates carbonyl or carboxyl groups on the surface of the carbon black as shown in Figure 1. Anhydride or lactone functions are found to react

further with H₂O. Oxidation leads to a decrease of the pH value of aqueous dispersions of carbon black.

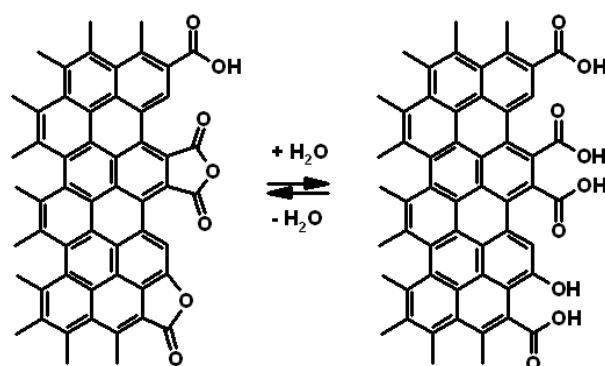


Figure 1. Oxidative generated groups

The most important physico-chemical changes are the following:

1. Common increase of the specific surface
2. Strong increase of wettability
3. Higher content of volatile matter at 950°C

Carbon black also contains oxygen groups without after-treatment. The occurrence of these groups depend very much on the origin of the carbon black. Whereas carboxylic, phenolic and lactonic groups can be detected on the surface of typical gas blacks, typical furnace blacks bear basic oxides like pyrones.⁶

Oxidation, leads to a relatively wide spectrum of groups, however. It is not possible to generate only one specific structure.

Besides the well known oxidative treatment some other methods to modify the carbon black properties were developed. The common characteristics of all of these methods is the formation of a covalent chemical bond between the carbon black surface and the modifying agent. One can distinguish between two different types of reactants. The first group involves molecules with carbon-heteroatom bonds. Sulfonation is a typical representative of this group. The second group of modifying agents leads to the buildup of carbon-carbon bonds. Grafting monomers or polymer structures belong to this class.

Sulfonation, which was already mentioned is an alternative to oxidation in order to increase the wettability of pigments. A wide range of sulfonating agents and respective processes were published during the last thirty years. Due to the relatively low reactivity of carbon black drastic reaction conditions and high reactive sulfonating agents have to be used. Such Processes use oleum with or without sulfur trioxide^{7,8} or ammonium sulfate,⁹ followed by a neutralization step. Reaction temperatures and times vary from 50-450°C and 1hr to 2 days, respectively. Often oxidation occurs as a side reaction. Another drawback is the aggressiveness of the sulfonating agents.

The coupling of polymers and carbon black is known for over 30 years.¹⁰ A great number of papers dealing with grafting were published since the early seventies.¹¹

All the typical polymer reactions like anionic, cationic and radical polymerizations were carried out with carbon black as reactant. In the meantime it is possible to bind for example polystyrene-, polyether- and polyester structures to the carbon black-surface. The aromatic system as well as groups already existing created by special treatment act as starting points for the polymerization. Reactions leading to these pivotal groups can be oxidation, nitration followed by reduction, electrophilic substitution or radical trapping.¹¹

The polymerization of monomers from the carbon black surface or the coupling of complete polymers and carbon black provides the opportunity to create tailor-made products. In comparison to oxidation, there are more opportunities than the attachment of hydrophilic structures. It is also feasible to create hydrophobic or reactive groups. The carbon black surface can be aligned to specific medium properties like polarity.

A special case is the encapsulation of pigments without building up chemical bonds. The pigment, for example carbon black,¹² then is nucleating the polymer precipitation (Figure 2).

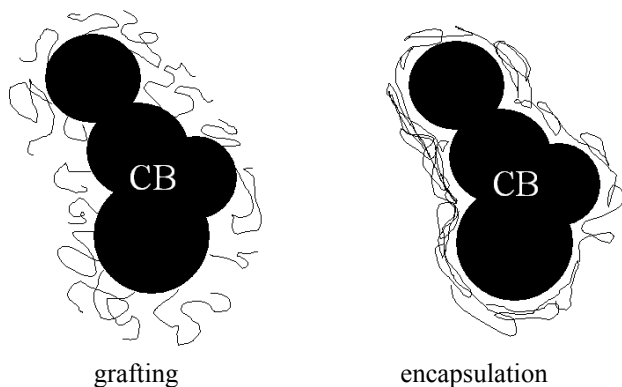


Figure 2. Grafted and encapsulated carbon black

Generally Van Der Waals interactions hold together the encapsulated pigment and the polymer. Without the firm attachment of the polymer to the carbon black surface via a chemical bond there is a risk that the polymer molecules

strip off, however. In this case adsorbed and unadsorbed polymers are in an equilibrium.

Different encapsulation techniques were developed. Particularly micro- and miniemulsion polymerizations lead to interesting products for NIP applications, especially for toner materials.¹³

Disadvantages of the carbon black modification with monomers or polymers are the necessity of several reaction steps, possible side reactions and the formation of large agglomerates.

Another way to generate chemical bonds between the aromatic system of carbon black and the carbon atom of a modifying agent accessible via Friedel-Crafts reactions.¹¹

The reaction of halogenated alkanes in the presence of Friedel-Crafts catalysts convert a relatively hydrophilic surface to very hydrophobic one. Acyl chloride-capped polyethyleneglycol is able to react with carbon black in terms of a Friedel-Crafts acylation.¹⁴

Another approach takes advantage of the reaction between carbon black and diazonium salts^{15,16} at elevated temperatures or electrochemically conditions. Because of the high reactivity of the diazonium salts several reaction mechanisms can occur (figure 3).

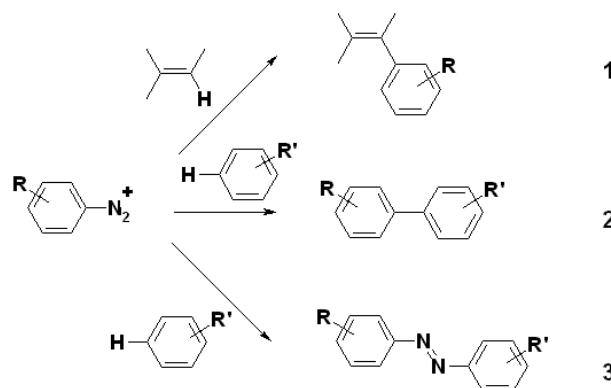


Figure 3. Reaction mechanisms of diazonium salts

Mechanism 1 corresponds to a Meerwein arylation. It requires an electron-deficient substituted double bond system. Closely related is mechanism 2, a typical Gomberg-Bachmann reaction. Both mechanisms proceed through radical intermediates after nitrogen is cleaved off.¹⁷

With corresponding substitution an azo coupling reaction can also take place (mechanism 3). This reaction which needs high temperatures is likely to give low yields due to the strong nitrogen separation. Other side reactions possible are the formation of phenols and halogenides in the presence of water or halogen salt.

In general this reaction can be carried out with a wide range of diazonium salts. It is possible to attach hydrophilic, hydrophobic, or other groups to the carbon black surface. For diazonium salts bearing hydrophobic groups the use of solvents is necessary. The use of solvents for the carbon black modification, however, may cause safety risks and leads to higher cost.

2. Carbon Black Modification on the Base of Cyclic Reactions

Degussa recently developed a new carbon black modification method utilizing the special electronic properties of the carbon black backbone.

Cyclic reactions are widely established for the generation of carbon-carbon bonds. Especially the [4+2] cyclo-addition has grown to an important instrument in preparative organic chemistry.¹⁸

The basic concept is the reaction of an activated carbon-carbon double bond with a diene system. Figure 4 shows a typical example of the Diels-Alder reaction.

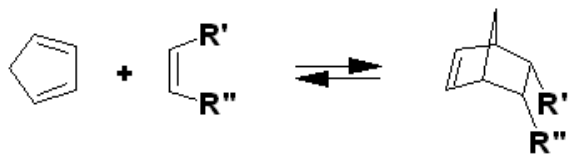


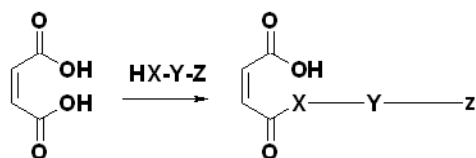
Figure 4. Diels-Alder reaction scheme

The Diels-Alder reaction is not limited to mono-annulated hydrocarbons. The rate constant increases on linear annelation. Hexacene reacts 1450 times faster than anthracene, according with Clar's sextet rule.¹⁹

Carbon blacks exhibit vast annelated π -systems. These regions can be understood as potential anchors to attach dienophiles. Because of the extended delocalization of the π -electrons, which corresponds to a state of low energy the dienophiles have to bear electron-withdrawing substituents. This property is offered by maleic acid derivatives like maleic anhydride, esters, amides and imides. Altogether these reactions systems are characterized by the following advantages:

1. High Diels-Alder reactivity
2. Unlimited substituents diversity
3. Simple preparation methods under mild conditions with good yields

Maleic acid and the maleic derivatives belong to the highly reactive dienes. They react with most dienes at room temperature. In some cases the temperature can be even lowered down to -70°C . Only special dienophiles like tetracyanoethylene or aza analogues of maleic anhydride show greater rate constants.²⁰ In these cases the substitution potential is very limited, however. Raw materials, which are comparably inexpensive and available in bulk quantities are maleic acid, its anhydride, and the respective aliphatic alcohols, phenols or amines (Figure 5).



anchor—spacer—property carrier

Figure 5. Synthesis of maleic acid derivatives

The substituent X can be an amino or a hydroxyl group leading to amides or esters. When X stands for HN- it is possible to transform the amide into a cyclic maleic imide with a higher Diels-Alder reactivity. The amide and especially the imide bonds are also harder to cleave than the ester bond. Aromatic or alkyl groups are able to act as fragment Y. Y allows the attachment of the functionality Z to the anchor and it acts as a spacer which has an advantage for several applications. It is then Z, which should be connected with the carbon black. This can effect higher wettability, enhanced hydrophobicity or a special polarity. The great number of organic molecules bearing the structural constitution HX-Y-Z are examples for the second point of the list mentioned above.

Another group of reactive dienophiles is acetylene derivatives.

Some typical examples of the reaction of carbon black and maleic acid derivatives are summarized in Table 1.^{21,22}

Table 1. Examples of the carbon black modification with maleic acid derivatives

Modifying agent (X=NH)		carbon black	yield [%]
Y	Z		
C ₆ H ₄	-OC ₆ H ₅	FW 1	35*
C ₆ H ₄	-SO ₃ Na	FW1	65*
C ₁₂ H ₂₅		Px 35	90**
NaOOC-C≡C-COOH		FW1	75*

* ratio carbon black : modifying agent = 5 : 1

** ratio carbon black : modifying agent = 15 : 1

The specific reaction conditions depend on the modifying agent.²¹ In some cases it is not necessary to work with solvents, which is a big advantage regarding both process safety and production cost.

IR and NMR-spectroscopy as well as TGA-MS and DSC are suited for the characterization of the modified carbon black. The Diels-Alder reaction makes it possible to synthesize the same basic carbon black with strong hydrophilic and hydrophobic properties. Figure 6 illustrates this remarkable difference in properties. Raw materials in this case were FW1 from Degussa and maleic acid monododecylamide (see table 1).

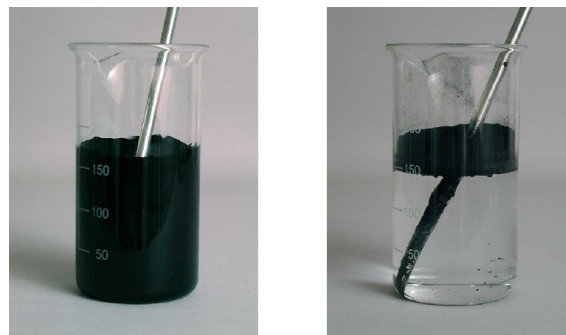


Figure 6. Hydrophilic / hydrophobic carbon black in water

The modification increases clearly the hydrophobicity (right picture: modified carbon black) in comparison to the unmodified carbon black (left picture).

3. Carbon Black Modification with Sulfur Containing Radicals

A new carbon black modification method taking advantage of special types of radical formers was developed by Degussa.

The ability to add radicals to the aromatic systems increases with the number of annelated rings. For instance the methyl radical affinity for naphthalene, anthracene and carbon black equals 80 to 790 to 10^7 . Mainly oxygen or nitrogen radical initiators like benzoyl peroxide or azobisisobutyronitrile were applied up to now.¹¹

While the synthesis and storage of these substances is difficult, the production of sulfur containing radical formers like disulfides is quite common, and manifold substituents are available.

This modification method also offers a wide spectrum of possibilities to influence the carbon black properties (see table 2²³).

Table 2. Examples of the carbon black Px 35 with disulfides

Modifying agent (R-S-S-R)	Solvent	yield [%]
R= CH ₃ -(CH ₂) ₁₁	-	>90
R= CH ₂ -Phenyl	toluene	60-90
R= Phenyl-pNH ₂	-	50
R= Phenyl-pSO ₃ Na	water	95

Disulfides fit the general modification agent scheme (Anchor→Spacer→Property Carrier) shown above with the advantage, that one molecule contains two units (figure 7).

The synthesis is very simple and effective. After the reaction with the carbon black the surface bears thioether structures.

Conclusion

The different modification methods established in the past few years open up the way to new types of tailor-made carbon blacks.

Especially two new flexible Degussa processes provide the opportunity to attach a great variety of chemical groups to the carbon black surface. The property changes shown in this paper are an indication of the potential of the new Degussa modification methods. Due to the easily accessible modification agents, together with the procedural advantages the surface properties of carbon blacks can be adjusted precisely to the special demands of customer systems.

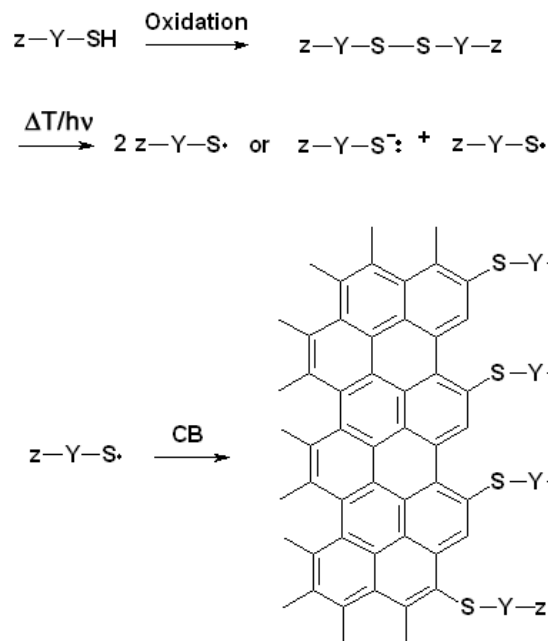


Figure 7. Synthesis of disulfides and carbon black modification with disulfides

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Biography

Dr. Thomas Lühge received his Ph.D. in Chemistry from the Martin-Luther-University Halle-Wittenberg in 2000. After one year post-doctoral work with Degussa AG he joined the staff of Degussa's application technology center, Advanced Fillers & Pigments. The focus of his work is on the detailed characterization of the chemical properties and the tailor-made modification of carbon black for NIP applications.