

## 4. PLASMA TREATMENTS

### 4.1 Introduction to Carbon Black treatment

Modification of CB has been used since a long time in order to improve final properties and behaviour of this carbon powders as already has been presented in chapter 3. CB reinforcing applications have tried to maximize the interaction between the filler and the polymer chain in order to obtain optimal final performance. But not only in this field CB can play an important role, previously mentioned in the introduction of this work, other applications such as the use of CB in inks and pigments and the use of CB as catalyst support for electrochemical reactions have also used this approach in order to improve performance.

Some of the treatments that have been described to have been carried out to modify CB surface, both by means of wet/gas chemistry as well as using plasma techniques, are here described. Two main treatment groups can be presented; one corresponds to the grafting of polymer chains and polymer deposition on the surface of CB. The other corresponds to the functionalization of CB surface which involves including on the CB structure other elements than C such as oxygen, nitrogen, fluorine, chlorine among others. Although a variety of modifications on CB have been described there is still a lack of production of modified CB at industrial level utilising economical and environmental sustainable processes.

#### 4.1.1 Grafting and polymer deposition on CB

Grafting on CB using wet techniques has been studied by several research groups. The group of Tsubokawa et al. have reported several techniques that can be used in order to graft polymer chains on the surface of CB, in most cases the reactions sites are the carboxylic groups present at the surface of channel CB's but can be also introduced on other CB types as it will be explained further on. Graft processes are based in radical or ionic addition polymerization. (N.Tsubokawa et al. 1985 and S. Hayashi et al 1998).

The groups of E.Papier and A.Vidal studied the effect of grafting chains with increasing C atom number ( $C_1$  to  $C_{16}$ ). In this case, CB was tested also for its reinforcement capability in NR and SBR at 50 phr. Although rheology experiments showed a better dispersion of the modified filler due to a decrease of the tixotropic phenomena, the final mechanical properties were not improved. The effect is explained by the coverage of the most energetic sites of CB by the grafted chains, which prevented the chains from the polymeric matrix to interact with the filler (E.Papier et al. 1990 and Vidal et al. 1991)

In the reinforcement field, the idea to graft silane molecules to the surface of CB has also been studied. Silanes are used successfully to diminish the interaction between silica particles and in some cases link them covalently to the polymer matrix. This process improves dramatically the performance of the final rubber goods (M.J. Wang 1999). However, this does not seem to be the case when CB is used as filler. Results reported by Wang et al. show that although some of the silane was chemisorbed on the surface of CB, most of it was only physisorbed on the most energetic zones of CB, probably due to the lack of functional groups on CB able to react with the silane (W.D. Wang et al. 1994). Similar results were presented by H.G. Yoon et al., who modified CB with aminopropyltrimethoxysilane and trimethoxy-n-propylsilane. Changes in the dispersion were observed also in this case, but once again improvements in the mechanical properties were not noticeable (H. Yoon et al. 2004). In both cases the blocking of the most reactive sites on CB due to the grafting process prevented good interaction with the polymer matrix.

CB grafting has also been applied in other fields, Cabot Corporation has proposed the modification of CB in order to improve its behaviour in water and organic based inks. The modification consists in linking an ionic group to the surface of CB by means of an organic spacer. Changing the ionic group as well as the length of the organic spacer the surface of CB can be tuned to obtain optimal dispersion and suspension in coating formulations (J. Belmont and C. Adams, 1997). Recently, K. Bergemann et al. reported CB modification of CB surface by reaction with maleic acid derivatives (at 180°C 4-5 hours). The final hydrophilicity of CB could be tuned as a function of the used derivative and therefore interaction with several solvents could be adjusted. (Bergemann et al. 2004)

It has to be pointed out however, that the presented modifications are often time consuming, from 5 to 10 hours, and they also need a washing step of the unreacted reagents as well as a drying step before the modified filler can be used in final applications.

Concerning plasma modification techniques very few grafting and polymerization deposition treatments on the surface of CB have been reported. Some attempts have been carried out by our research group in order to modify CB surface by plasma polymerization with acrylic acid (AA) as reactive monomer (N. Tricas 2001). CB was modified in a Bell-Jar reactor type at 40W during 60 minutes at 0.2 mbar. The pH of CB decreased from 7.5 to 4 after the deposition of AA, on the other hand the structure of CB remained unchanged as measured by Raman Spectroscopy it can be observed in Fig.4. 1. When the surface energy was evaluated by means of IGC, both dispersive as well as specific component were diminished as it can be seen in Table 4. 1.

Table 4. 1 Surface Energy for Unmodified CB and after acrylic acid deposition

|               | Total Surface energy<br>(mJ/m <sup>2</sup> ) | Dispersive Component<br>$\gamma_s^d$ (mJ/m <sup>2</sup> ) | Specific component<br>$\gamma_s^{sp}$ (mJ·m <sup>-2</sup> ) |
|---------------|--|---|---|
| Unmodified CB | 778  | 608   | 170   |
| AA-CB         | 333  | 250   | 83  |

The results obtained from filled compounds showed that the polymer deposition decreased the CB reinforcement power. This effect was attributed, as it was in the previous cases, to the coverage of the CB surface active sites which were unable to interact with the polymer. On the other hand the deposited polymer did not have enough long chain to cause entanglements with the polymer matrix. As a consequence the reinforcement capacity of CB was diminished down by a decrease of a 10% of the bound rubber level.

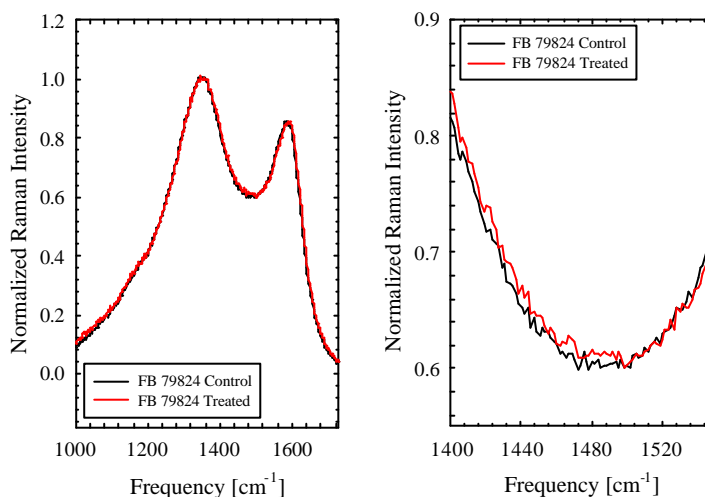


Fig.4. 1 Raman Spectra of unmodified CB and after Acrylic Acid deposition by cold plasma

Dynamic mechanical analysis showed a decrease in the dispersion degree which could be due to a higher filler-filler interaction and consequently as it has been proposed a lower polymer-filler interaction. This effect can be observed in Fig.4. 2

The effect of CB coverage to the detriment of CB reinforcement ability was also observed by G. Akovali et al. after modifying CB with styrene and butadiene vapour plasma, plasma conditions being RF (13,56MHz) 30 W during 30 minutes at 1 mbar (G. Akovali et al. 1999).

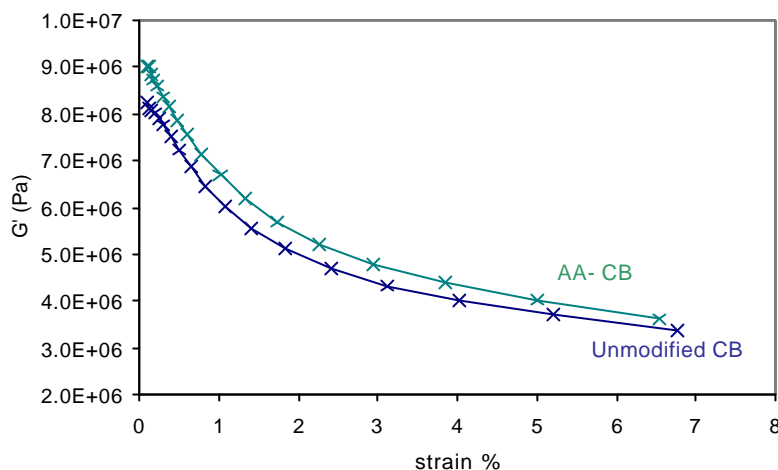


Fig.4. 2  $G'$  measurement at low strain for 50ph NR compounds

On the other hand, plasma polymer deposition using  $C_2F_6$  as plasma reactive monomer was used in order to cover CB at 40W for 60 minutes at 0.8 mbar, RF (13.56MHz). CB was used thereafter as Platinum support for oxygen reduction reaction. Improvement in the reaction rate as well as in the platinum live length as catalyst were detected, the hydrophobicity as well as the affected electronic state of the Pt particles are thought to be a consequence of the  $CF_3$  groups introduced on the CB surface (H. Shioyama et al. 2006)

As a conclusion it can be said that CB grafting and polymer deposition, although it can be very useful in coating applications helping to improve CB dispersion in different media and change the final polarity, it does not seem to be useful for reinforcing applications. This result is a consequence of the coverage of the high energetic sites which play a very important role in the filler-polymer interaction. Therefore, other approaches such as trying to functionalize CB surface without annihilating the high energy sites could be interesting in order to improve CB behaviour in this application.

#### 4.1.2 Functionalization of CB

The present work deals mainly with carbon black functionalization and therefore more information about previous works will be given. Some of the modifications studied on the CB surface have been only carried out in order to gain some insight into the surface and interior of carbon black structures while others search for a performance improvement. The functionalization treatments have been divided in three main groups: oxidation, nitration and other performed functionalization treatments.

#### 4.1.2.1. CB Oxidation

Oxidation of CB has been widely studied in order to change its hydrophilicity but also as mentioned above, in order to elucidate CB structure by means of studying the reaction of oxygen with the different structures present on the CB surface. This was the case of one of the earliest work presented by Heckman et al. where CB was progressively oxidised in hot air (Heckmann et al 1966). It was observed that CB particles oxidation took place preferably in the bulk meaning that the bulk portion was more susceptible to burn. As a consequence it was assumed that the inner part of the particle was formed by less ordered carbon structure than the surface. This hypothesis was much latter confirmed by SANS experiments (R. Hjelm et al. 2000)

From that time on, many oxidation treatments on Carbon Black have been described using several oxidizing agents such as acid medium such as HNO<sub>3</sub>, ozone, KOH hydrogen peroxide among others (Vidal et. al. 1972, Y. Otake et al 1993, E.Papier et al. 1996, S.J. Park et al. 2001). Although all these treatments increased successfully the level of oxygen on the surface of CB, they also produce changes on the surface structure and morphology of CB. Many times the use of the same oxidation reagent has reported controversial results about the changes produced in specific surface area and microporosity. For example N. Krishanankutty et al. reported that CB presented a lower specific surface area and lower microporosity after being modified with HNO<sub>3</sub> (15.8N during 6 hours) (N. Krishanankutty et al. 1995) . A drastic decrease of specific surface area was also reported by S.J. Park et al after H<sub>3</sub>PO<sub>4</sub> modification (S.J. Park et al. 2000). However, other groups have described that specific surface area remained at a constant value after HNO<sub>3</sub> (0.3M at 95°C for 6 hours) modification or even increased due to microporosity formation (R.C. Sosa et al. 1966).

Oxidation by hot air, has also reported and increase of the oxygen content on the CB surface and similar results as the ones obtained for HNO<sub>3</sub> (15.8N during 6 hours at 100°C) oxidation (P.E. Fanning et al. 1992, X.Chen et al. 2003), but in some occasions a decrease of the total oxygen content on CB surface was described (R.C. Sosa et al. 1996). The group of Chen et al. studied also the difference between Ozone and molecular oxygen, while molecular oxygen is though to attack only selective positions such as crystallite edges, ozone seems to attack the whole surface. The same study showed that while molecular oxygen produced an increase of the specific surface area, due to microporosity formation, it remained unchanged after the ozone treatment (X. Chen et al.2003). Other ozone modification studies showed that specific surface area decreases for treatments below 150°C but increased for higher temperatures (Z.B. Wang et al. 2006).

Therefore, a clear mechanism of the oxidation process has not been elucidated and the influence of the reaction parameters such as acid concentration, reaction duration, CB grade and temperature among others seem to be crucial to obtain reproducibility and avoid CB structure and morphology changes.

On the other hand, oxidized CB has been tested in many applications. Already in 1969 G.R. Cotten utilized ozone/air and  $\text{HNO}_3$  (at  $120^\circ\text{C}$ ) oxidized CB in order to observe changes in SBR rubber compound properties. The obtained results showed that, in both cases, oxygen present at the CB surface diminished the maximum torque obtained in the vulcanization curve ( $M_H$ ) which is probably related to a lower cross-link degree, decreasing at the same time the velocity of the vulcanization reaction (G.R. Cotten et al. 1969).

Later on, during the 90's several research groups studied the effect of oxidized CB in several polymer matrixes. J.A. Belmont et al. Introduced oxygen functionalities on the CB surface by reacting phosphines and phosphates, it is thought that peroxide groups are introduced on the surface of CB during the reaction. Final properties of filled BR were improved. However, because phosphines solutions are air sensitive, experiments must be carried out under inert atmosphere (J.A. Belmont et al, 1991). Several works studied the interaction of CB in polymer matrixes containing oxygen groups such as epoxydated Natural Rubber and carboxylated nitrile rubber (A. Roychoudhury 1995, S. Bandyopadhyay 1995 and A.K. Mana et al 1997). In some cases the use of a silane coupling agent was also evaluated (A.K. Mana et al. 1992). Improvements were found when the CB loading was higher than 80 phr, on the other and an optimal silane content was 4phr as higher amounts provoked plasticizing effects. In 1998 it was proved that oxygen on the CB surface decreased the crosslink levels when BR was vulcanized in a peroxide system, probably due to the interaction of the peroxide compound with the oxygen groups on the surface of CB. However, it was found that submitting the Br filled with oxidized CB to high temperature and pressure, known as High Pressure Vulcanization (HPV), increased the polymer adsorption on the CB known as bound rubber in a 39% (Bellander et al. 1998)

Contrary to the grafting process, CB functionalization seems to have a positive effect in reinforcing applications. This effect depends on the polarity of the polymer matrix and the interaction with other ingredients of the compound formulation.

CB oxidation seems also a good way to improve electrochemical properties of CB, R.C. Sosa et al. oxidised CB with several reagents such as  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$  hot air and humid ozone. The first two methods increased the surface oxygen content and increased the surface negative charge. As a consequence the adsorbed catalase and iron porphyrines can preserve a higher planarity and therefore a higher activity for  $\text{H}_2\text{O}_2$  decomposition is observed. Treatment with hot air did not produce an increase of surface oxygen, while when using humid ozone the oxygen concentration increased for short periods and subsequently decreased (R.C. Sosa et al 1996). Carbon black and carbon filaments have also been modified with hot air and acid medium ( $\text{HCl}$  and  $\text{HNO}_3$ ) in order to improve the electrochemical behaviour of these materials by C.A. Frysz et al. (C.A. Frysz et al. 1997). Oxidation induced reversibility to the studied reaction  $\text{Fe}(\text{CN})_6^{-3/-4}$  being the hot air process the one giving best performance. Ozone was used by Z.B Wang et al. to improve the

activity of Pt supported catalyst for oxygen reduction in DMFC. Modification studies were performed in a temperature range from 60 to 180°C. (Z.B. Wang et al. 2006) Optimal treatment to increase platinum activity was 6 minutes at 140°C.

As last presented application it has to be said that wet oxidation of CB's has been also used by many companies (Cabot Corporation, Degussa, Columbian Carbon among others) in order to improve its dispersion in water solvent inks, as it can be found described in several Patents (M. Masayuki and K. Miharu 2004, P. J. Melore and F. J. Eckert 1966, W. Kalbitz and A. Karl 2001 and K. Suetsugu and E. Maruyama 1976)

It seems that from all presented studies, wet oxidising treatments produce oxidation in preferential positions of the carbon black surface, including amorphous structures and crystalline edges, while basal graphitic planes only react at very aggressive conditions that provoke severe changes in the CB particle. On the other hand, the use of ozone in gas state seems to provoke an homogeneous oxidation with lower structural changes.

The use of oxygen plasma in order to modify CB surface is also well-known. However, one of the main points in that has been studied and still not hundred percent clarified is whether oxidation of CB in plasma oxygen species attack preferential sites on Carbon black such as crystallite edges, or if the oxidation in the plasma is a non-preferential attack.

The group of Tascon et al. have studied in detail the oxidation process in a microwave plasma reactor as was explained in chapter 2. Although the reactor was not specially adapted to treat powders and very small amounts of treated material were processed, some very interesting results have been presented. CB was treated at 2.45 GHz, 150W for 35 min. A comparative study using oxygen plasma and molecular oxygen on several carbon types showed that reactivity is different in both media, while molecular oxygen oxidizes preferably activated carbon showing a higher reactivity with non-crystalline structures, plasma oxidation was very reactive with carbon black giving a hint that oxygen plasma could modify the graphitic structures. This hypothesis was confirmed by the successful modification of graphitized CB using oxygen plasma (L.E. de Torre et al 1998 and A.Cuesta et al. 2001). A later study using STM and AFM made it possible the observation of the CB after oxygen plasma showing an homogeneous treatment all over the particle (J.I. Paredes et al. 2005). Graphitised CB modification with oxygen plasma was also studied by the group of Donnet et al. in a RF (13.56MHz) at 1.3 mbar 75 W and 30 min. Surface energy studies showed that both dispersive and specific energy components were modified during the oxygen plasma treatment. The surface was also studied using STM where disruption of the surface crystallinity was observed (J.B. Donnet et al. 1994 and W. Wang et al. 1993)

T. Takada et al. used a RF reactor at 13.56MHz 50W at different treatment durations (from 5 to 480 min) to study also CB oxidation. It was shown that oxygen increases for the first

120 minutes of treatment increasing the total weight of the carbon, however after that time oxygen content decreases provoking also carbon gasification. The main functionalities found were C=O, O-C-O and O-C=O (T.Takada et al. 1996)

The use of plasma oxidised CB has also been tested in several applications. X.Li et al. showed how the electrochemical properties of CB were improved after plasma oxidation as tested by H<sub>2</sub>O<sub>2</sub> decomposition capability. As presented in chapter 3 (3.1.1.1), this group used a RF (13.56 MHz) Bell-Jar reactor where CB was deposited in a vibrating tray. Reaction took place at 15W during 10 minutes (X. Li et al. 1999).

In the reinforcement field, S.J. Park et al. studied the influence of oxygen plasma treatment in a RF reactor (13.56 MHz) of CB in the mechanical properties of carbon black rubber (NBR) composites. Although the modification system of CB is not described, plasma conditions were 60W from 0 to 130 minutes (S.J. Park et al 2003). Results show that a higher filler-polymer interaction is obtained for the modified filler.

Therefore, it can be said that oxygen plasma seems indeed a good way to introduce oxygen species on CB surface without producing other important changes. However, it has to be pointed out that no continuous or APP treatments have been described and that can be detrimental for a production in the industrial scale.

#### 4.1.2.2 Carbon Black Nitrogen Enrichment

Surface nitration and amination and nitration is a quite common topic on polymer surfaces in order to enhance polymer adhesion (M.Creatore et al. 2001) as well as in the biomaterial field where biocompatibility and cell adhesion are two of the main requirements (K. Schröder et al. 2001). As it was described in chapter 3 it has been also widely studied on polymer powders using plasma modification (F.Bretagnol et al. 2004). However, this modification has not been deeply studied on carbon materials. As a matter of fact very few information can be found about this topic when referred to carbon black, some works are presented next.

In 1999 modification with N<sub>2</sub>O<sub>3</sub>, NO and N<sub>2</sub>O<sub>4</sub> was used by F. Cataldo to introduce nitro and nitroso groups on the surface of CB. CB structure remained unmodified as shown by the Raman Spectroscopy measurements while an increase of fraction of polymer chains adsorbed on the CB was increased (F. Cataldo 1999). Although the hysteresis of the final rubber compound was reduced the formation of nitrosamines when using certain accelerator systems should be carefully studied.

Very few works are also found about for plasma treatment on carbon surfaces in order to include nitrogen and nitrogenated functionalities. In this case some early work from I.H. Loh reports the use of ammonia plasma, nitrogen and nitrogen/hydrogen mixtures on CB.



In this case the modification was done in a stationary reactor and the influence of the position of the powder in the plasma region was studied. Modification with ammonia plasma was done at 100W during 30 minutes using 0.1g of carbon black at 1mbar. A mixture of  $N_2:H_2$  was also used (1:2) at the same conditions; however the nitrogen content on the final surface was in this case lower than when using ammonia plasma. Adsorption with ammonia was carried out to confirm that nitrogen was covalently bonded to the carbon surface, it was observed that after ammonia adsorption no nitrogen could be detected on the surface of CB. It has to be pointed out that in all cases after modification the content of nitrogen on the surface of CB decreased with time ( I.H. Loh et al. 1987).

More recently, S.J. Park et al. used also nitrogen plasma in order to modify the CB surface, in this case an RF (13,56 MHz) reactor at 30W from 0 to 30 minutes at 1mbar. Structural, changes in the surface crystallinity, and energetic changes are observed (S.J. Park et al 2001) but no applications are evaluated in this work.

S.Kima et al. used nitrogen plasma to modify CB utilised as support for platinum catalyst in Direct Methanol Fuel Cells (DMFC). CB was modified in an RF (13.56 MHz) at 300W. 30 seconds was found to be the optimal treatment duration in order to increase Platinum activity towards methanol oxidation. New functional groups on the CB surface were found to be: C–N, C=N,  $-NH_3^+$ ,  $-NH$ , and  $=NH$  (S. Kima et al 2006).

Last but not least, the group of P. Favia et al. studied the modification of CB granules in a plasma containing different proportions of  $NH_3$  and  $O_2$ . 20W and 100W treatments at 0.25mbar were performed (P. Favia et al. 2006). CB treated at 100W contained lower functionality levels than the ones modified at 20 W. Acid and base values of modified CB changed consistently with plasma composition.

It has to be said that ammonia plasma has been commonly used to modify other carbon powders such as carbon nanotubes (CNT) and Carbon nanofibres. Using a low pressure Microwave generated plasma reactor (2.45 GHz) in a power range from 25 to 100W and a treatment time 20 to 40 minutes CNT were modified in an ammonia plasma by B.N. Khare et al. (B.N. Khare et al. 2004). An increase of Nitrogen functionalities is observed after the modification is observed, C=N and N-H bonds are observed after 20 minutes of treatment. On the other hand the group of A. Felten et al. modified CNT in an RF (13.56MHz) LPP reactor at 30W and 0.1 mbar during 30 minutes. Nitrogen groups such as imine, amine, nitrile and amide groups were found on the CNT surface after modification (A.Felten et al. 2004). V.Brüser et al modified carbon nanofibres in a rotary reactor at 0.01 mbar using  $NH_3$ , no dependence on plasma power was found between 50 and 80W while nitrogen content decreased when the pressure was lower than 0.01 mbar (V. Brüser et al 2004)

#### 4.1.2.3. Other CB functionalization treatments

At this point other treatments that have been described on CB but that are not so much related with the work here developed are presented. Although species are different they can also offer some insight in the effect of CB surface on modification both when being modified by wet and plasma techniques.

Attempts of introducing sulphurated species on the surface of CB have also been described. In this case the presence of the sulphur on the CB surface was expected to take part in the crosslinking by sulphur vulcanization. First results were presented by Papier et al. who studied the introduction of sulphur at the surface of CB and oxidised CB using  $\text{ClSO}_3\text{H}$  and  $\text{C}_4\text{H}_9\text{SH}$  (E. Papier et al 1978). Final sulphur increase was below 0.15% of the initial content. Later studies by Gajewski et al. showed a higher crosslink density and better tear properties for high sulphur content at the CB surface (up to 6%) CB was modified by means of  $\text{S}_8$ ,  $\text{CS}_2$ ,  $\text{SO}_2$ , and  $\text{H}_2\text{S}$ , being the most reactive  $\text{SO}_2$  and the less  $\text{H}_2\text{S}$  (M. Gajewski et al. 1994).

Introduction of heteroatoms on the surface of CB has also been studied. For example, the group of Tressaud et al. studied in detail de Fluorination of CB surface. Reaction conditions have been studied % of  $\text{F}_2$  gas and pre-treatment of the material with  $\text{O}_2$  that increases the final content of F on the CB surface. The carbon surface structure was found (G. Nansé et al. 1997a, 1997 b and 1997c). Similar studies were performed by the same group in  $\text{CF}_4$  plasma using an RF (13.56Mhz) using a power range from 40 to 100W and a treatment duration between 10 and 30 minutes. Also under these conditions fluorination was found to be dependent on CB structure, more crystalline structure favoured the formation of fluorine graphite while higher disordered structures promoted the formation of  $\text{CF}_x$  groups (A. Tressaud et al. 2002).

Other heteroatoms such as Cl and Br have been also introduced on the surface of CB. Br was introduced by using liquid reagents ( $\text{Br}_2$  dissolved in  $\text{CCl}_4$ ) and bromine vapours at  $120^\circ\text{C}$ . It was found that the brominated groups present on the surface was dependent on the bromination method (P.Eugene et al. 1994). A similar method was used to introduce Cl on the CB surface, bubbling  $\text{Cl}_2$  through  $\text{CCl}_4$  and thereafter the mixture is carried over the CB at  $450^\circ\text{C}$  (E.Papier et al. 1996) In both cases specific surface energy component was increased while a 6.7% of bromine and 6.9% of chlorine were introduced on the CB surface.

As a conclusion of the presented summary of modification of CB it can be said that although surface functionalization to introduce oxygen groups has been widely applied, the lack of continuous processes is still to solve. This work will deal with the use of APP to produce oxygen groups on the surface of CB. The changes produced will be compared with LPP modification. On the other hand the lack of information about CB nitration both

with nitrogen and ammonia has led to bring a deeper insight into this process both at LPP and APP pressure plasma. Finally, a combination of both treatments has also been evaluated.

Although due to technical reasons, the same plasma parameters such as gas composition, plasma power and treatment time could not be used in both systems, conditions were set up to obtain similar modifications in both cases and therefore compare the capability for each method. As a summary three different treatments can be highlighted; oxidation of carbon black by means of oxygen and air treatment, basification of carbon black by means of ammonia plasma and combination of a pre-treatment of oxygen treatment followed by an ammonia plasma treatment, and finally nitrogen introduction on the CB surface by means of nitrogen plasma.

Details of the performed treatments and nomenclature for further result discussion are given next.

### **4.2 Performed Treatments at LPP**

As above mentioned three main treatments were carried out using the LPP reactor. In the case of LPP pure oxygen was used in order to carry out oxidation, a mixture of ammonia and argon was used in order to introduce basic groups while pure nitrogen was used with the finality to introduce N groups. It is also worth to mention that 15 g of CB were used in each batch, although higher amounts are also possible to treat (up to 30g), 15g were considered the amount with an optimal fluidization inside the reactor.

In order to study and optimise the plasma conditions for each type of treatment, oxygen, nitrogen and ammonia in this system, N134 has been used as reference material. Using this CB several conditions were tested as will be indicated below. Once the conditions were optimized, they were also utilised to modify the following CB grades: N134, N134g, N134e, XPB 171 and Vulcan.

In order to give a reference to these treated carbons the following nomenclature was used:

CB grade\_plasma gas\_c

Letter c at the end stands for cold plasma, although both plasmas used during this study are not thermal, traditional nomenclature and also a true temperature variation between LPP and APP is present. An example for a treated carbon should be:

Vulcan\_N<sub>2</sub>\_c

In the case where oxygen plasma pre-treatment is carried out before ammonia plasma the nomenclature will be as following:

Vulcan\_O<sub>2</sub>\_NH<sub>3</sub>\_c

When necessary further information about the treating conditions will be given in each section. However, a complete list of the performed treatments is given below.

LPP Treatments on N134 as reference material for optimization:

#### 4.2.1 Oxygen LPP Treatment:

Oxygen LPP treatment was carried out on N134, pure oxygen was supplied by Carburos Metálicos with 99,999% purity. Background pressure was held at  $2 \cdot 10^{-2}$  mbar and at 0,2mbar during operation conditions. Oxygen plasma presented a clear blue colour. Time and generator power were the variable parameters as shown in Table 4. 2, with a total of 5 experimental conditions :

Table 4. 2 Experimental conditions for O<sub>2</sub> LPP modification

| Time (min) | Power (W) |
|------------|-----------|
| 5          | 40        |
| 10         | 40        |
| 15         | 40        |
| 20         | 40        |
| 30         | 40        |

#### 4.2.2 Ammonia Plasma LPP Treatment:

Ammonia LPP treatments were conducted with a mixture of NH<sub>3</sub>:Ar (ratio 3:1). Gases were also supplied by Carburos Metálicos, Ar 99,999 and NH<sub>3</sub> C50 (maximum purity). Plasma colour was yellow in the middle were probably more active species such as NH<sub>2</sub><sup>+</sup>, NH<sub>3</sub><sup>+</sup>, were present and purple due to the Ar and also N<sub>2</sub> (N<sub>2</sub><sup>+</sup>, N<sup>+</sup>, N<sub>2</sub><sup>\*</sup>) species around. Background pressure was held at  $2 \cdot 10^{-2}$  mbar and 0,3 during modification conditions With a total of 20 different experimental conditions.

Table 4. 3 Experimental conditions for NH<sub>3</sub> LPP modifcaiton

| Time (min) | Power (W)   |
|------------|-------------|
| 10         | 20/40/60/80 |
| 20         | 20/40/60/80 |
| 30         | 20/40/60/80 |
| 40         | 20/40/60/80 |
| 50         | 20/40/60/80 |

#### 4.2.3 Nitrogen Plasma Treatment LPP:

Finally, for nitrogen modifications gas was also supplied by Carbueros Metálicos with a 99,999% purity. Plasma colour was orange at low powers (15W) going to pink at higher ones. (80W) Conditions evaluated for this type of treatment are presented in the table below with a total of 7 trials to fins optimal process.

Table 4. 4 Experimental conditions for N<sub>2</sub> LPP modifcaiton

| Time (min) | Power (W) |
|------------|-----------|
| 15         | 15/30     |
| 30         | 15/30/80  |
| 60         | 15        |

After evaluation of the materials obtained from the experiments above, which will be discussed further on in this work, following conditions were determined to be utilised to treat the rest of CB grades:

Table 4. 5 Conditions used after optimization for O<sub>2</sub>, NH<sub>3</sub> and N<sub>2</sub> LPP treatments

| Plasma Gas | Time (min) | Power (W) |
|------------|------------|-----------|
| Oxygen     | 15         | 40        |
| Ammonia    | 30         | 40        |
| Nitrogen   | 30         | 40        |

Before all treatments the reactor was purged with the treatment gas after achieving the background pressure. The treatment gas was introduced in the system and pressure was allowed to reach 100 mbar, afterwards the flow was adjusted to obtain the treatment pressure and system was stabilized 10 minutes before the treatment started. In order to finish the treatment, the generator was stopped at the same time than the plasma flow. Background pressure was again achieved to remove any species left in the reactor. In the case of oxygen treated samples, the system was filled with atmospheric air in order to

remove vacuum, in the case of nitrogen and ammonia treated carbons, the reactor was filled with nitrogen and left about 30 minutes to minimize post-reaction with atmospheric oxygen.

In the cases where a pre-treatment with oxygen plasma was done before the final ammonia plasma treatment, conditions for the oxidation pre-treatment were also the ones detailed above.

### **4.3 Performed Treatments at APP**

Similar treatments than the ones described for LPP were also carried out at APP conditions. However, due to working conditions operations at atmospheric pressure, the plasma system was only able to generate plasma with air and nitrogen. Therefore, air plasma was used in order to produce oxidative changes on the surface of CB while nitrogen plasma was used to introduce nitrogen functionalities. In order to obtain basic surface groups, a post-treatment injecting ammonia at 40mm from the plasma nozzle origin as described in ch.3. (3.2.2) was used.

In this case also N134 was used as a reference material to test the parameters in the APP system. However because very limited changes could be introduced in the generator and time parameters, other variables were established to study the system.

- Plasma Gas: the gas going through the plasma nozzle where plasma is generated: nitrogen and air were used separately to modify the CB surface
- Number of cycles through the reactor: because CB was calculated to be in the plasma region only in the millisecond range, the effect of CB going through the reactor repeatedly was studied both with the oxygen and nitrogen plasma
- CB inlet position from the plasma nozzle: initially, the influence of entering CB at two different positions in the system, one at 5 mm and the other at 10mm of the plasma nozzle, was evaluated.

About 100 grams were produced for each time of treatment and the samples were named as indicated here:

CB grade\_plasma gas\_a

Where letter a at the end stands for atmospheric pressure. An example is given below-

N134\_air\_a

In the case where ammonia was used as post-reactive gas the reference is presented as:

N134\_(N<sub>2</sub>+NH<sub>3</sub>)\_a

And finally those pretreated samples with air plasma before treatment with (N<sub>2</sub>+NH<sub>3</sub>) are described as:

N134\_air\_(N<sub>2</sub>+NH<sub>3</sub>)\_a

The parameters used in each treatment (cycle numbers and inlet distance), will be indicated in each section. However some relevant information as well as a treatment overview is given here next.

#### 4.3.1 Air Plasma at APP

Compressed air in-situ was used in order to generate the air plasma. Although shown in ch. 3 (3.2.2) during the gas analysis, the system could work in a range of flow controlled by an exit manometer at the compressed air exit. It was decided to fix the manometer at where the plasma flame showed a more stable behaviour (2 bar).

#### 4.3.2 Nitrogen Plasma at APP

In this case of nitrogen, the system was purged with the nitrogen for 10 minutes in order to ensure the elimination of oxygen in the system which could favour the oxidation process instead the nitrogenation.

#### 4.3.3 Ammonia post reaction at APP

Ammonia as explained previously was introduced through an inlet positioned 40mm downstream from the beginning of the plasma flame. Ammonia was provided by Linde at maximum purity. A flow meter (rotameter type) was used in order to control the flow which was varied between 0,5 and 2 L/h.

Table 4. 6 presents the 9 experiences that were carried out during the optimization and evaluation of the effects of the studied variables in the APP system using N134.

Table 4. 6 Studied Parameters during APP modification for N134

| CB    | Plasma Gas                      | # Cycles | CB inlet position (mm) | NH <sub>3</sub> Flow (L/h) |
|-------|---------------------------------|----------|------------------------|----------------------------|
| N-134 | Air                             | 1        | 5                      | 0                          |
| N-134 | Air                             | 1        | 10                     | 0                          |
| N-134 | Air                             | 2        | 10                     | 0                          |
| N-134 | N <sub>2</sub>                  | 1        | 10                     | 0                          |
| N-134 | N <sub>2</sub>                  | 2        | 10                     | 0                          |
| N-134 | N <sub>2</sub>                  | 1        | 5                      | 0                          |
| N-134 | N <sub>2</sub> +NH <sub>3</sub> | 1        | 10                     | 0,5                        |
| N-134 | N <sub>2</sub> +NH <sub>3</sub> | 1        | 10                     | 1                          |
| N-134 | N <sub>2</sub> +NH <sub>3</sub> | 1        | 10                     | 2                          |

In the case of APP modification only two CB were used: N-134 and XPB171. Only fluffy CB that could be fluidized in the air and blown into the system without blocking the system was suitable to be modified in the system. In this case the two CB's presenting a very different specific surface area and microporosity are expected to give important information of the influence of these parameters during the plasma treatment.

The treatments performed using XPB 171 were the ones presented at table X. Conditions were selected from the analysis of the N134 samples obtained after

Table 4. 7 Studied Parameters during APP modification for XPB 171

| CB     | Plasma Gas                      | # Cycles | CB inlet position | Ammonia Flow (L/h) |
|--------|---------------------------------|----------|-------------------|--------------------|
| XPB171 | Air                             | 1        | 10                | 0                  |
| XPB171 | Air                             | 2        | 10                | 0                  |
| XPB171 | N <sub>2</sub>                  | 1        | 10                | 0                  |
| XPB171 | N <sub>2</sub> +NH <sub>3</sub> | 1        | 10                | 2                  |

To this point both the plasma systems as well as the plasma conditions that have been used during this work have been presented. The capabilities of both system in order to produce oxygen and nitrogen (both by nitrogen plasma and ammonia plasma conditions) groups will be evaluated in the next chapter. Not less important the use of several CB's will give the opportunity to study the influence of the initial CB surface.



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