8. CONCLUSIONS

1. Concerning the set-up and optimization of plasma reactors at both low and atmospheric pressure the following conclusions are presented:

   - A down-stream reactor has been redesigned for LPP modification of powder materials. The vacuum exit was relocated to improve powder stirring and vacuum system protection. The reactive gas inlet was carefully positioned thanks to its flexible configuration that allows surface modification of the materials down, in and up-stream of the plasma generation zone. The reactor was found suitable to treat powders in the nanometric range such as fluffy CB, at a load between 15 and 30 grams per batch. Working conditions in terms of treatment time and power were optimized for oxygen, nitrogen and ammonia treatment of CB powders.

   - A fluidized bed reactor for LPP of powders has been designed. The reactor has shown its versatility in terms of plasma relative position to the sample, size and shape of the treated powder. However, more experiments should be done in order to use this type of reactor in order to modify fluffy CB as it low apparent density and small size prevented to obtain a good fluidization behavior.

   - An APP device has been successfully designed in order to be connected to a commercial AP torch from Plasmatreat GmbH. The reactor is able to treat 1-3 g of CB/min of fluffy CB depending on the velocity of the carrier gas in an almost continuous way. The influence of treatment parameters such as number of treatment cycles through the system or distance of the CB inlet to the plasma torch have been studied for air and nitrogen plasma.

2. After characterization of the modified CB powders at the different reactors, down-stream LPP and APP torch, it can be concluded:

   - No morphological relevant changes in terms of specific surface area and microporosity were detected after any of the performed treatments on the different selected CBs. This fact indicates that the modification takes place only in the very surface layer of such material. This is confirmed by the results obtained by means of XRD and WAXS techniques which show modification of CB surface crystallinity.

- Focusing on the oxidative functionalization treatments it was observed that a higher number of acid miliequivalents per gram of CB were introduced on the CB surface by means of APP treatment. This is due to a generalized modification of the total exposed CB surface area by the air APP treatment. On the other hand, oxygen plasma treatment reactivity showed to be more sensitive to CB surface properties such as chemical composition, microporosity and surface structure showing preferential reaction with aromatic impurities present on N134 and graphitic planes obtained after N134 graphitization.

- As far as CB nitrogen enrichment is concerned, best results were obtained by means of nitrogen APP treatment on N134 which increased nitrogen composition up to 1,7%, and 0,5 % for XPB 171. In this case the modification degree is not proportional to surface area. On the other hand, when LPP was utilized on N-134 for such finality, nitrogen pure plasma (60 W/30min) and ammonia:argon (40W/30min) treatments show similar nitrogen final content: 0,4% and 0.35% respectively. There is also evidence that the nitrogen plasma may cause some surface ablation creating high energy dispersive sites which might have and important role in the final behavior. It was also observed that ammonia LPP reacts easily with CBs presenting high amorphous carbon content such as extracted N134 and consequently no modification for graphitized N134 was observed. XPS analysis revealed pyridinic nitrogen to be the main functionality for the nitrogen atoms introduced both during LPP and APP treatment.

3. From the studies focused on CB reinforcement ability, based on the influence of CB surface treatment on vulcanization reaction and the CB-polymer interaction some relevant observations are presented.

- Air APP treated CB has been found to alter the CBS decomposition mechanism and the final properties of BR rubber compounds. The phenomena was not so strongly developed in NBR compounds probably due to a better interaction of CBS and the polymer matrix, which prevented the accelerator to strongly interact with the CB surface.

- On the other hand, MCV had permitted to corroborate the importance of both the CB structure and chemical composition during the CBS decomposition. Amorphous carbon on the surface (or amorphous –crystallite edges) is proposed to be the site where the decomposition of CBS is catalyzed. On the other hand, the presence of polar groups created by APP catalyze the CBS decomposition but at the same time change the reaction mechanism due to early MTBT formation during the reaction. Not less important, nitrogen APP treated CB obtains a faster CBS decomposition without changing the final product of the reaction and improving the final rubber properties.

- It has also been seen that the surface modification also altered the polymer-filler interaction both by increasing Butadiene rubber bound rubber and polymer adsorption from solution. However, sever care has to be given to the presence of other compounds that may compete for such adsorption positions.

4. As a conclusion for the study based on modified CB as support for non-noble metal oxygen reduction catalyst, it can be established that many parameters play a key role in order to obtain high activity ORR catalysts from nitrogen and iron precursors on carbon materials. Following the carbon characteristics which have been found to have a higher influence are presented:

- Initial Carbon Structure: N134 graphitization prevented the carbon to become active. Possible surface structure changes caused by plasma activation may also benefit the final activity of the catalyst (e.i. air APP plasma)

- Initial N content: Increase of nitrogen percentage by means of plasma techniques both LPP and APP has been shown to increase the final ORR activity of the treated surface. On the other hand CB surfaces that presented low reactivity towards plasma modification presented also low ORR catalyzation abilities.

- Carbon reactivity during pyrolisis: It has been corroborated that those CB's presenting higher weight losses during pyrolisis do also present higher ORR catalysis. However, it is not a linear relation and a maximum catalytic activity is obtained at 40%.

- Final microporosity: Increase in microporosity during the pyrolisis have also been related to the obtainment of higher activity level of ORR catalysts. Although a small number of samples were tested a linear relation was obtained when relating this increase with final Vpr value obtained by means of cyclic voltammetry.

- On the other hand, no evidence of the influence of other parameters such as final nitrogen concentration or final pyridinic nitrogen on the carbon surface were found as determinant parameters as was stated by other previous works.