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TESI DOCTORAL

Títol PLASMA MODIFICATION OF CARBON BLACK SURFACE: FROM REACTOR DESIGN TO FINAL APPLICATIONS

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SUMMARY

The present works deals with plasma modification of carbon black (CB). Although this type of treatment is widely used on flat surfaces handling problems should be overcome in order to treat powders as CB. In this study CB has been modified both by means of low-pressure and atmospheric pressure non-equilibrium plasmas. In order to accomplish this objective three different plasma reactors have been set-up; two at low pressure and one at atmospheric pressure working conditions.

Low pressure plasma reactors utilised in this work consist in a down-stream and a fluidised bed system working at Radio Frequency generation power (RF 13,56 MHz). Both reactors have been optimized to treat powder materials. For the down-stream reactor, position of the reactive gas inlet, and treatment conditions such as generator power and time have been studied for oxygen, nitrogen and ammonia treatments. For the fluidized bed reactor the distance of the powder sample to the plasma generation zone, particle size and support porosity have been taken into account.

Concerning atmospheric plasma, a device has been set up in order to adapt a commercial plasma torch (Openair® from Plasmatreat GmbH), for powder modification. An adaptable reactor, a method to introduce the powder in the plasma zone as well as a collecting system had been developed in order to obtain a quasi-continuous modification treatment.

Three types of CBs, N134, XPB 171 and Vulcan XC-72 have been modified in both the down-stream and the atmospheric plasma system. Graphitization and extraction of N134 were also carried out before plasma modification in order to study the effect of both impurities and surface structure of the CB during plasma modification. Surface oxidation and nitrogen enrichment were the two main studied treatments in both systems which allowed comparing their performances.

Unmodified and Modified CBs have been characterised from several points of view. Specific surface area, XRD, WAXS and STM have been used in order to study morphological and surface structure changes. On the other hand, pH measurements, acid/base titration and XPS were employed in order to study the surface chemistry composition changes that had taken place during plasma modification.

Some of the modified CB grades were selected in order to be tested in final applications such as rubber reinforcement and oxygen reduction non-noble metal catalyst for PEMFC. In the first case, the effect of atmospheric plasma treatment on the vulcanization kinetics and mechanism has been evaluated both by rheometre curves and the model compounding approach. Studies about the polymer-filler interaction have been also carried out by calculating bound rubber and adsorption from polymer solution. Last but not least, plasma modification capacity to enhance the oxygen reduction activity to obtain non-noble metal catalysts for PEMFC has been evaluated after the correspondent preparation. Oxygen reduction activity has been studied by means of cyclic voltammetry. The main CB properties which could play an important role in such applications have been analyzed.

1. INTRODUCTION

Carbon Black (CB) has been used for a long time as a reinforcing filler in rubber applications. Since S.C. Mote discovered by chance its good reinforcement properties when he decided to mix it with rubber, carbon black has been mainly used as tire reinforcement filler. Still today, Carbon black is used in an 80% in the tire industry but other applications are also becoming popular. The use of CB as pigment in inks or carbon conductive support in catalysis application should also be pointed out.

In all previous mentioned applications it is important to remark that carbon black is in contact with very different media and it is rarely used on its own. As a consequence of being in contact with other substances, carbon black surface properties play a very important role on its final performance in any of its applications as will be further presented.

For example when mixed with polymer, carbon black should be able to disperse and have a very good interaction with the polymer molecules, which have mainly unpolar nature. Although the reinforcement mechanism has still not been clarified after many years of study, the influence of specific surface area, structure and surface energy, also known as surface activity, have been reported (A.I. Medalia 1973, G. Kraus 1965). It is known that the better the interaction between polymer and carbon black, the better is the dispersion of the filler and also the mechanical properties of the final goods. On the other hand when filler particles trend to agglomerate, they make the dispersion process much more difficult and lead to very poor performance properties (B.B.Boonstra 1966, M.J. Wang 1998 and M. Gerspacher et al. 1998). For many years carbon black seemed to be the only option as reinforcement filler and no other competitors were on the market. The appearance on the scene of modified silica with improved surface activity, which provided better dispersion and rubber interaction, has been threatening CB industry which should also start developing new CB with enhanced surface properties (W.D. Wang et al. 1994).

When used in inks, carbon black is dispersed normally in polar solvents and is expected to be able to keep in suspension for long periods. In order to do so, CB should present enough water affinity and surface charges so that it is able to stay in the solution. If the dispersion is not well stabilized, CB could settle causing final surface imperfection. Small particle size and high polar carbons, mainly obtained by ozone treatment, are normally used for this finality.

Finally, the third example presented is the use of carbon black as support for catalysts, this is the case of the reactions taking place at fuels cells (S. Mukejee and S. Srinivasan 2003). For this finality Carbon black is coated with platinum where the reaction takes place, and it is responsible to conduct the generated electricity to the external circuit. In this case carbon should have not only a good adhesion with platinum but also a high gas and water wettability as the reaction takes place in a three state system. Highly conductive CB's are the choice in this field. But CB can not only improve the platinum efficiency, it has also been described that after appropriate modification CB could be able to include oxygen reduction sites on its surface (G. Lalande and J.P. Dodelet 1995 and M. Lefévre and J.P Dodelet 2000). These structures resemble the cytocrome C placed in the human cells and could be a candidate to eliminate the use of Platinum, being expensive and rare, as catalyst for oxygen reduction in massive application of fuel cells.

Therefore, the presented examples confirm that although carbon black is a very interesting material due to its high surface area, structure, colour, and conductivity among other properties, the interaction with the surroundings is a key factor in order to achieve optimal results in each different scenario. As a consequence, the performance of CB is determined to a large extent by its surface and interfacial properties.

The surface activity of carbon black is one of the main driving forces of carbon black interaction properties. This property is very close related to its surface chemical composition and surface microstructure as it is here described. Since the 60's several models have been proposed to explain the microstructure and surface energy heterogeneity of CB surface and still today an extended accepted description of CB surface has not been found. However, it has to be said that, although the actual models may not agree in all points, it is generally accepted that the surface of carbon black is composed by different carbon structures related to different energy levels. One of the most known models is based on the presence of graphite crystallites and amorphous carbon zones. The most highly energetic sites are described as the crystallite edges, followed by the amorphous carbon and finally the graphite planes (A. Schröeder et al. 2002).

Concerning CB surface chemistry, some years ago it was believed that the chemical groups (mainly oxygenated groups) present on the surface of carbon black, could have also an important role in the carbon black interaction capacity with molecules. Nowadays, the furnace process used to produce carbon black does not give the carbon surface the opportunity to get oxidized, and therefore, the presence of other elements other than carbon on the surface of CB can be neglected. This argument leads to the conclusion that differences in behaviour between different carbon black furnace grades are not due to a different surface chemical composition. This hypothesis was confirmed by our research group when it was observed that two CB's belonging to the same ASTM grade (N-660), but produced in different reactor, could have different surface behaviour as noticed during the vulcanization reaction. It was confirmed by means of X-Ray Photoelectronic Spectroscopy that the CB surface chemical composition was the same for the two CB's showing different activity (J. Clotet 2005). On the other hand, it should not be forgotten that some functional groups can be introduced on the carbon black surface after the production. The most common used techniques are gas and wet treatments in order to change CB hydrophobicity and reactivity (G.R. Cotten et al. 1969, J.B. Donnet et al. 1972, G. Nansé et al. 1993, E. Papier et al. 1996).

As a conclusion it can be said that the surface activity is the total surface energy which includes the energy not only related to carbon structure but also the one due to the chemical functional groups present on the CB surface. As it is the case for all solid surfaces, free energy of carbon black (γs) can be defined as a sum of two different components, each one corresponding to a specific type of interaction:

$$g_s = g_s^d + g_s^{sp} \qquad \text{eq.1.1}$$

In the above energy equation g_s^d corresponds to the dispersive component of the surface free energy (mainly due to Van der Waals interaction between different molecules), which in this case would be related to the different carbon zones. The higher the number of crystallite edges the higher the value of the dispersion component. On the other hand g_s^{sp} is the sum of the specific components of the surface free energy (which involves dipole-dipole and induced dipole-dipole, as well as hydrogen bonding and acid-base interactions), and increases strongly with the amount of polar surface groups. These two energetic components, which are directly related with the surface activity, are responsible for the behavior of CB in different media. As a consequence it seems possible and challenging that by tailoring surface activity of carbon black the best surface properties for each application could be obtained. This surface modification would include both a carbon surface structure change as well as a chemical composition modification.

Different ways of changing surface activities of carbon black have already been described, including graphitization processes at high temperature, wet chemical treatments, gas chemical reactions and although may be not so deeply studied cold plasma treatments have also been reported (I.H. Loh 1978, E. Papier et al. 1994, T.W. Zerda et al. 2000, S.J. Park et al. 2001a and 2001b). However, this last type of treatment it seems a very promising technique due to its unique properties and will be the one used during the present work as it is here presented. Plasma is known for being a very reactive media which is able to produce graphting, ablation, ion implantation and polymer deposition on surfaces (H. Yasuda, 1985). Although it is usually applied on flat surfaces it can be also applied on powder materials when adequate systems are used (F. Arefi-Khonsari 2005, C.Arpagaus 2005, P. Favia et al. 2006). However, the low pressure reactors used in most cases are not as much interesting from the industry point of view, as it would be a continuous atmospheric, but unfortunately, this type of system need still to be much further developed (VDI Technologiezentrum GmbH, 2004).

Due to the exposed facts, the aim of this work is to modify the surface activity of carbon black (including surface structure as well as chemical composition), by using plasma techniques both at low and atmospheric pressure and study the effects of the modification on final CB applications. In order to achieve these objectives, following the working plan is presented.

1. Reactors set-up:

In order to be able to modify the carbon black different reactors both at low and atmospheric pressure need to be designed and optimized. These equipments provide the possibility to compare the carbon black treatment at different conditions.

In the case of low pressure conditions two different approaches using RF plasma will be evaluated for which a down-stream plasma reactor and a fluidized should be set up.

On the other hand, in the case of atmospheric plasma a commercial apparatus from Plasmatreat® GmbH will be adapted to treat powder material. In this case it has to be pointed out that this is the first time that such plasma equipment is used to modify powder materials.

2. Carbon Black Modification:

Once the different reactors are set up, several CB types (N-134, Vulcan XC72 and XPB 171) are treated under different working conditions which are here briefly described.

When treating CB with low pressure plasma the most important parameters to be studied are: reactive gas (O_2, N_2, NH_3), reaction time (10 to 60 min.) and plasma power (20 to 80W).

Due to a higher system complexity plasma gas (N_2 and air) is the main parameter which is modified during the atmospheric plasma treatment.

3. CB Characterization:

After submitting CB to the modification with the different plasma reactors CB is characterized in order to be able to study the effects of the treatment on the CB surface. This characterization will allow comparing the effect of each different treatment as well as the differences due to the type of reactor being used. CB surface will be analyzed in terms of surface microstructure, chemistry composition and surface energy.

4. Final Applications:

The final part of this work is focused in testing the modified material in final common applications such as rubber reinforcement and catalyst support.

In the first case the influence of the surface activity during the vulcanization reaction will be studied together with the polymer filler-interaction phenomena.

Last but not least, a very specific application will be evaluated. After the appropriate treatment, the activity of the material versus oxygen reduction is studied by means of

Cycling Voltametry and Rotating Disk Experiments. The results are correlated with the chemical surface composition, microporosity and microstructure properties.

REFERENCES:

- F. Arefi-Khonsari,. M.Tatoulian, F. Bretagnol, O.Bouloussa, F.Rondelez, Processing of polymers by plasma technologies. Surface and Coatings Technology 200 (2005) 14

- P. Favia; N. De Vietro,; R. Di Mundo,; F. Fracassi,; R.d'Agostino, Tuning the acid/base surface character of carbonaceous materials by means of cold plasma treatments. Plasma Processes and Polymers 3 (2006) 66

- C. Arpagaus, A.Rossi,; R. von Rohr, Short-time plasma surface modification of HDPE powder in a Plasma Downer Reactor - process, wettability improvement and ageing effects. Applied Surface Science 252 (2005) 1581

- B.B. Boonstra, Über das Mischen von Kautschuk und Russ, Wechselwirkung und Verstärkungs Mechanismus, Kautschuk Gummi und Kunststoffe, 4 (1996)198

- .J. Clotet, Estudio de la adsorción de acelerantes de vulcanización tipo sulfenamida sobre negros de carbono de distinta actividad superficial, Masther THesis, Institut Químic de Sarrià-Univarsitat Ramón Llull, Barcelona 2005.

- G.R. Cotten, B.B. Boonstra, D. Rivin and F.R. Williams, Effect if Chemical Modification of Carbon Black on its Behaviour in rubber Kautschuk Gummi und Kunststoffe 9 (1969) 477

- J. B Donnet, P.Ehrburger and A.Voet, Mechanism of the oxidation of carbon black by ozone in aqueous solution. Carbon 10 (1972) 737

- G. Kraus, *Reinforcement of Elastomers by Carbon Black*, Wiley Interscience, New York 1965

- G. Lalande, I. Côté, G. Tamizhmani, D. Guay, J. P. Dodelet, l. Dignard-bailey,l. T. Weng and P. Bertran, Physical, chemical and electrochemical characterization of heat-treated tetracarboxylic cobalt phthalocyanine adsorbed on carbon black as electrocatalyst for oxygen reduction in polymer electrolyte fuel cells , Electrochimica Acta 40 (1995) 2635

- M. Lefèvre and J. P. Dodelet P. Bertrand O_2 Reduction in PEM Fuel Cells: Activity and Active Site Structural Information for Catalysts Obtained by the Pyrolysis at High Temperature of Fe Precursors *Journal of Physical Chemistry B 104 (*2000) 11238

- I.H. Loh, R.E. Cohen, R.F. Baddour, Modification of carbon surface in cold plasmas, Journal of Materials Science 22 (1987) 2937

- A.I. Medalia, Elastic modulus of vulcanizates as related to carbon black structure. Rubber Chemistry and Technology 46 (1973) 877

- S. Mukejee and S. Srinivasan, Handbook of Fuel Cells- Fundamentals, Technology and Applications, Volume 2 Chapter 37, Edditors: W. Vielstich, H.A. Gesteiger and A. Lamm, John Wiley & Sons 2003.

- G. Nansé, E. Papirer, P. Fioux, F. Moguet and A. Tressaud Fluorination of carbon blacks. An X-ray photoelectron spectroscopy study. Part II. XPS study of a furnace carbon black treated with gaseous fluorine at temperatures below 100 °C. Influence of the reaction parameters and of the activation of the carbon black on the fluorine fixation Carbon 3 (1997) 371

- S.J Park, J.-S Kim Modifications produced by electrochemical treatments on carbon blacks. Microstructures and mechanical interfacial properties. Carbon 39 (2001a) 2011

- S.-J. Park and J.-S. Kim. Influence of Plasma Treatment on Microstructures and Acid-Base Surface Energetics of Nanostructured Carbon Blacks: N_2 Plasma Environment. Journal of Colloid and Interface Science 244 (2001b) 336

- E. Papier, R. Lacroix, and J. B. Donnet, Chemical modifications and surface properties of carbon blacks, Carbon 34 (1996)1521

- E. Papirer, R. Lacroix, J.B. Donnet, G. Nanse, Ph.Fioux, XPS study of the halogenation of carbon black. Part 1. Bromination. Carbon 32 (1994) 1341

- A.Schröder, M. Klüppel, J.Heidberg and R.H Schuster, Surface energy distribution of carbon black measured by static gas adsorption Carbon 40 (2002) 207

- VDI Technologiezentrum GmbH, *“Evaluierung Plasmatechnik“* Düsseldorf 2004.

- H.Yasuda, Plasma Polymerization, Academic Press London (1985)

- D.W. Wang , A. Vidal, G. Nause and J.B. Donnet, Kautschuk Gummi and Kunststoffe 47 (1994) 493

- M.J: Wang, Effect of Polymer-Filler and Filler-Filler interactions on dynamic properties of filled vulcanizates, Rubber Chemistry an Technology 71 (1998) 520

- T.W. Zerda and T. Gruber, Raman Study of Kinetics of Graphitization of Carbon Blacks Rubber Chemistry and Technology. 73 (2000) 284