

6. INFLUENCE OF CB SURFACE ON VULCANIZATION AND RUBBER PROPERTIES

One of the aims of this study was to examine which was the effect of CB surface treatment by plasma techniques on final applications. Two different fields have been chosen; in this chapter the reinforcing ability and the effect of the CB treatment on the vulcanization reaction are presented. In the last chapter (Ch.7), the effect of CB as possible non-noble metal catalyst for oxygen reduction will be studied.

6.1 Study of CB Role on Vulcanization

The so-called electrometric materials are characterized for their high elasticity, in other words, they are prone to suffer considerable deformation under stress but to recover their original dimensions once the stress is no longer applied (recovering the energy that was stored during the deformation period).

However, in order to avoid a permanent deformation due to the stress at which the material has been submitted, the polymer chains must be crosslinked preventing the slipping of the polymer chains (Fig.6. 1).

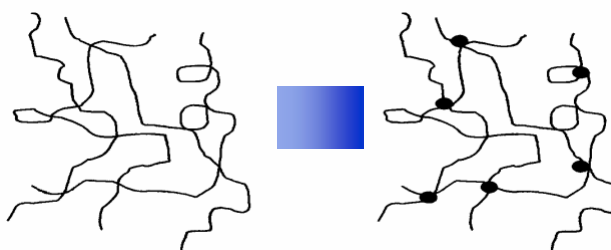


Fig.6. 1 Crosslinking process known as vulcanization or curing reaction

These unions between different polymer chains are essentially formed by the addition of sulfur, which at high temperatures give place to mono and polysulfidic bridges, essentially between different polymer molecules.

However if only sulfur is added, the crosslinking reaction is very slow and has a very poor efficiency. To solve this problem different compounds known as accelerators are added in the formulation. Each type of accelerator has a different effect on the vulcanization process which is shown in Fig.6. 2. A short scorch time but long enough to obtain an homogenate mixture and to avoid pre-vulcanization, as well as a fast reticulation kinetics, (related with the slope of the curve), and a high maximum torque which is somehow

related with the reticulation density, are the properties that would define the optimal accelerator.

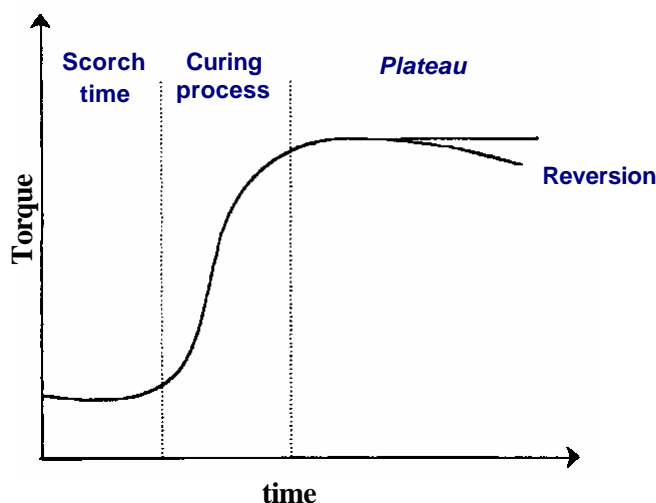


Fig.6. 2 Different steps of the vulcanization curve.

For many years although the crosslinking process and the use of fillers were known to be necessary to obtain good performance properties, the vulcanization reaction mechanism remained almost unstudied. However, the need to improve rubber materials leads to pay a special attention to the role of CB in vulcanization as well as to determine the parameters that have a major influence in this process.

Several techniques have been used in order to study the mentioned reaction and the effect of the present chemicals and fillers in the compound, rheometer curves, Model Compound Vulcanization (MCV), DSC and C^{13} RNM solid state are the most important (M. Porter et al. 1967, G.R. Cotten 1972, F. Lautenschlaeger et al. 1980, N. Agulló 1998, M. Mori and J.L. Koenig, 1995).

6.1.1 Rheometer Curves

One of the most used and easiest way to understand how the filler presence can alter the crosslinking reaction is monitoring the curing process in a rheometer, which has been used since many years (M. Porter et al. 1967). Interesting parameters such as the scorch time, the crosslink degree and the reaction kinetics can be obtained from this test. These parameters are presented in both Fig.6. 2 and Fig.6. 3. It is wide known that the presence of CB reduces the scorch time, also its role as a catalyst accelerating the reaction and obtaining higher reticulation level has also been accepted in many published papers although a specific mechanism has never been described (J.J. Brennan et al. 1972). However, studying reticulation level from the vulcanization curve maximum torque is not trivial, as in the presence of the filler, both the filler network as well as the sulfur unions

6. INFLUENCE OF CB SURFACE ON VULCANIZATION AND RUBBER PROPERTIES

contribute in the increase of this parameter. The rheometer is not capable to distinguish the two different components although some methodologies such as comparison with unfilled compounds have been used for a long time (G.R. Cotten 1972).

Table 6. 1 presents the main parameters that provide information about the reaction kinetics and the cross-link density that can be obtained from a rheometer curve. They are also represented in Fig.6. 3

Table 6. 1 Vulcanization parameters obtained from a rheometer curve

Parameter	Explanation
t_1	time in which there is an increase of 1% of the initial torque. It is usually taken to measure the scorch time.
t_{90}	time in which 90% of the final torque is reached. Is considered the optimal time for the rubber vulcanization as overheating the material could lead to reversion processes.
M_L	The minimum torque achieved during the vulcanization. I an indication of the material viscosity and can be related to the dispersion of the filler and its interaction with the polymer matrix
$M_H - M_L$	The difference between the maximum an the minimum torque, related to the crosslink density of the material although further detail for the evaluation will be given.

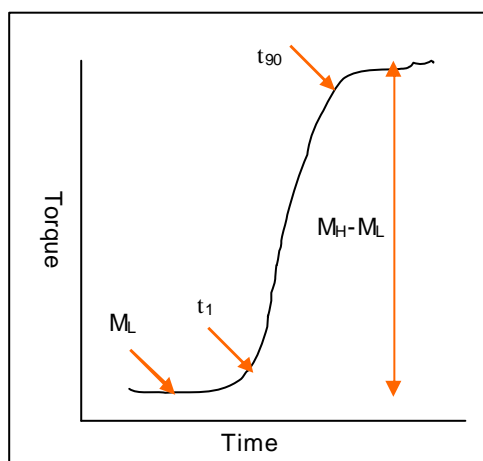


Fig.6. 3 Vulcanization Parameters on a rheometer curve

Although some studies have stated that only the CB loading and not its grade are responsible for the previous modifications, (M. Mori and J.L. Koenig, 1997), other results show that there are some other variables that need to be taken into account such as the CB surface chemical nature. Concerning vulcanization kinetics, Cotten has observed that the crosslinking rate constant decreases when the acid concentration on the CB surface increases, some CB structural dependence was also found (G.R. Cotten, 1972 and 1979).

It was also observed that oxidized CB by means of HNO_3 and ozone did not only reduce the vulcanization kinetics but also decreased the MH-ML value indicating a lower crosslink capability when NR was vulcanized by CBS-sulfur system. The effect was not observed when SBR was vulcanized with the same curing system and oxidized black neither when TMTD was used as accelerator. However, no explanation for such effect was given (G.R. Cotten et al. 1979).

Finally is also worth to mention that S.J. Park studied the vulcanization reaction of a SBR filled with modified CB (KOH and C_6H_6 already presented during this work) by means of rheometer curves. They stated that the changes produced by the CB modification altered both the vulcanization reaction and the final properties of the material. They found that KOH modified CB with higher specific energy component than unmodified CB, accelerated the vulcanization kinetics but same MH was reached. On the other hand C_6H_6 modified carbon with higher specific dispersive component, although it did not accelerate the reaction higher MH values were obtained as well as better behavior in the strain-stress curves (S.J. Park et al. 2005)

6.1.2 Model Compound Vulcanization (MCV)

Most of the previous described techniques though, require a difficult sample preparation and manipulation when working with rubber. This is the reason why MCV (Model Compound Vulcanization) approach, which consists in substituting the polymer by a similar low weight compound, is still considered today a useful tool to study polymer reactions and interactions. Different models for some polymers such as natural rubber, butyl rubber, SBR or EPDM have been described in literature. However, it is worth to point out that to obtain reliable results using the MCV approach a suitable low weight molecule must be chosen. The molecule structure and the number of reactive sites are the two main variables to take into account.

After the vulcanization reaction with the chosen molecule, the products present in the mixture should be analyzed. The low molecular weight of these molecules, making them soluble even after their crosslinking, allows using a wider range of analysis techniques facilitating their study.

Table 6. 2 Molecules used as Model COmpound for vulcanization studies

Nº	Name	Nº	Name
1	Geraniol	7	2,3-dimethyl-2-butene
2	Geraniol	8	Cycloocten-1,5-diene
3	Squalene	9	Cyclohexadeca-1,5,9,13-tetraene
4	Cyclohexene	10	Trans-3-hexene
5	2-methyl-2-pentene	11	1-decene
6	ethylidene norbornene	12	2,3-dimethyl-1-butene

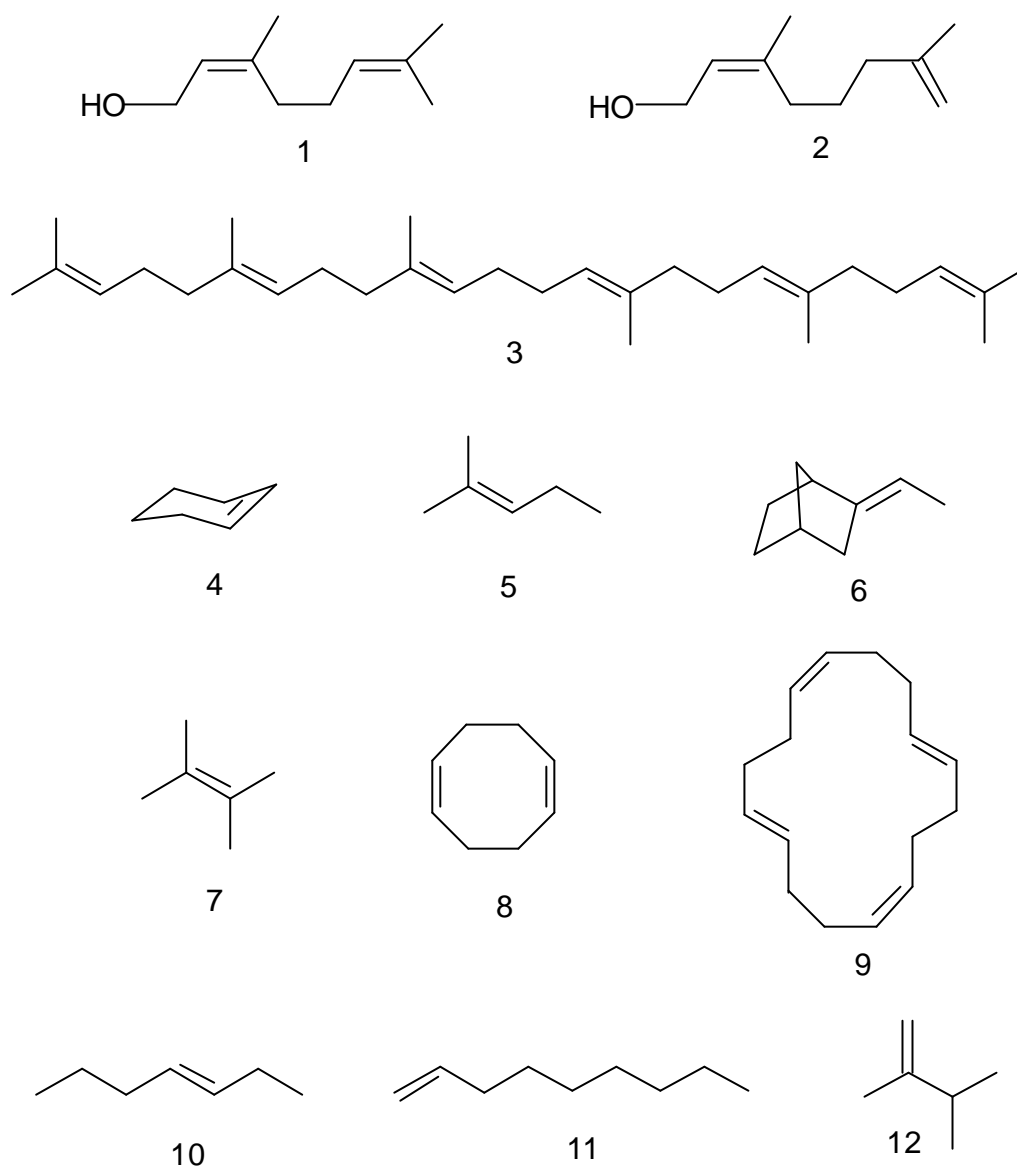


Fig.6. 4 Compounds used as models of different elastomers

HPLC is one of the analytical techniques used for both the separation and identification of the present compounds during MCV vulcanization reaction. With this technique it is possible to follow the accelerator decomposition, its intermediates and final products, as well as the resulting compounds of the model molecule crosslinking. Using this technique, studies on the vulcanization of natural rubber using squalene as a model molecule, and CBS as accelerator, have been performed in our research group which determined the decomposition path of the accelerator to give reactive species (N. Agulló 1998). The reaction path for EPDM vulcanization was studied by the research group of DSM using also the model compound approach (J. H. M. Van Den Berg, 1984).

But MCV can not only be used to study vulcanization mechanisms but also the influence of chemicals and filler on the reaction path, such as antireversion agents, silane coupling agents and fillers (F. Lautenschlaeger 1980, P. J. C. Van Haeren 1996, P. Versloot 1997). Concerning CB influence on the vulcanization not much work has been reported. Studies on CB influence were performed by our research group using ToF-SIMS as analysis technique to study adsorbed compounds on CB during and after squalene vulcanization. The fact that the reaction compounds are present on the CB surface can also cause the vulcanization reaction to preferably take place in this location and play a very relevant role during the crosslink formation (S. Borrós and N. Agulló, 2000, E. Vidal et al. 2002 E. Vidal-Escales and S. Borrós, 2002).

Although MCV can be very useful for the study of vulcanization reaction mechanism and kinetics, some controversy is also present when results should be extrapolated to long polymeric chains. Different processes could take place in a solid matrix than in a liquid media.

6.1.3 Other techniques to study vulcanization reaction

Other analytical tools have also been used to confirm the CB effects on the vulcanization. The group of McGill vulcanized polyisoprene with TMTD (tetramethyltiuram disulfide), in presence of CB in a DSC, to follow the reaction samples at different times were collected and analyzed by HPLC. The conclusion was that the reaction mechanism was not altered but confirmed the scorch time decrease as well as an increase of the crosslink formation rate as a result of the catalytic effect of CB on TMTD polysulfurated species (W.J. McGill and S.R. Shelver, 1995).

On the other hand, Koenig et al. using ^{13}C solid state NMR measurements observed that CB might affect the vulcanization mechanism. They suggested that the basic network structure formation could be modified due to crosslink desulfurization from poly to monosulfide structures. This higher level of monosulfidic unions has also been stated as the reason why CB filled polymers are more resistant to reversion (M. Mori and J.L. Koenig, 1995).

In addition, other studies with ^{13}C NMR and ^1H transversal relaxation solid state measurements were done on CB filled natural rubber vulcanizates to determine the chemical cross-link density, (G. Simon and A. Wutzler, 1992). In this case increasing the filler loading seems to decrease the cross-link density. The authors explained that this effect could be a consequence of the adsorption of curatives on the filler surface, as well as a reduction of the polymer chains mobility. Such contradictory results make it evident that there is still much to learn about this subject.

As it has been presented although several techniques might be used in order to assess the role played by CB during the vulcanization reaction, it is difficult to find a unique

method that can provide with enough information about the influence of CB. Therefore, in this work two of the presented approaches; rheometer curves and MCV using squalene as a model have been used as complementary techniques in order to study the effect of CB plasma modification on the vulcanization reaction.

6.1.4 Results by Rheometer Studies

In this section, the rheometer curves for APP treated CBs are presented in order to study their effect in the vulcanization reaction. To fulfill this objective modified N134 by APP techniques with both air and nitrogen plasma were used in order to prepare rubber compounds. N134 CB was selected as it is the one used for this type of application while atmospheric treatment was the one preferred due to the large amounts needed both for the trials or in a real application.

However, in this study also 3 experimental CB's from Sid Richardson Carbon Co (A1, A2, A3) were also included. These CBs which are also rubber grades and which present a tailored surface structure while specific surface is very similar in all cases, therefore there were used in order to study the effect of CB surface structure in the vulcanization reaction.

In all cases the following procedure was used in order to obtain the rubber compounds. Curing sulfur semi-efficient systems shown in Table 6. 3 were incorporated in the previous to several polymer matrixes.

Table 6. 3 Used recipe for the studied compounds amount are given in phr.

Polymer	CB	Sulfur	CBS	ZnO	Stearic acid
100	Variable	1.7	2.5	2.5	1

Mixtures were made in a laboratory scale inner mixer. Temperature was set at 60°C and rotor speed at 50rpm. Each compound was prepared following the next procedure for a total of 12 minutes:

- First two minutes polymer alone was mixed
- CB is added and mixed for next 8 minutes
- Vulcanization system is added and mixed for the last 2 minutes

In order to verify the final content of the filler in the compound a TGA analysis was carried out. All compounds were found to differ less than 2%. An example for a comparative TGA for NBR mixtures is given in Fig.6. 5.

Rheometer curves were obtained at 160°C in a Monsanto rheometer using a 1.667Hz frequency and 0.5° strain. Studied parameters include t_1 as scorch time, t_{90} as final vulcanization time, M_L as initial viscosity and M_H-M_L . M_H-M_L was considered the final

crosslink density as the same amount of CB was included in the formulation for all mixtures.

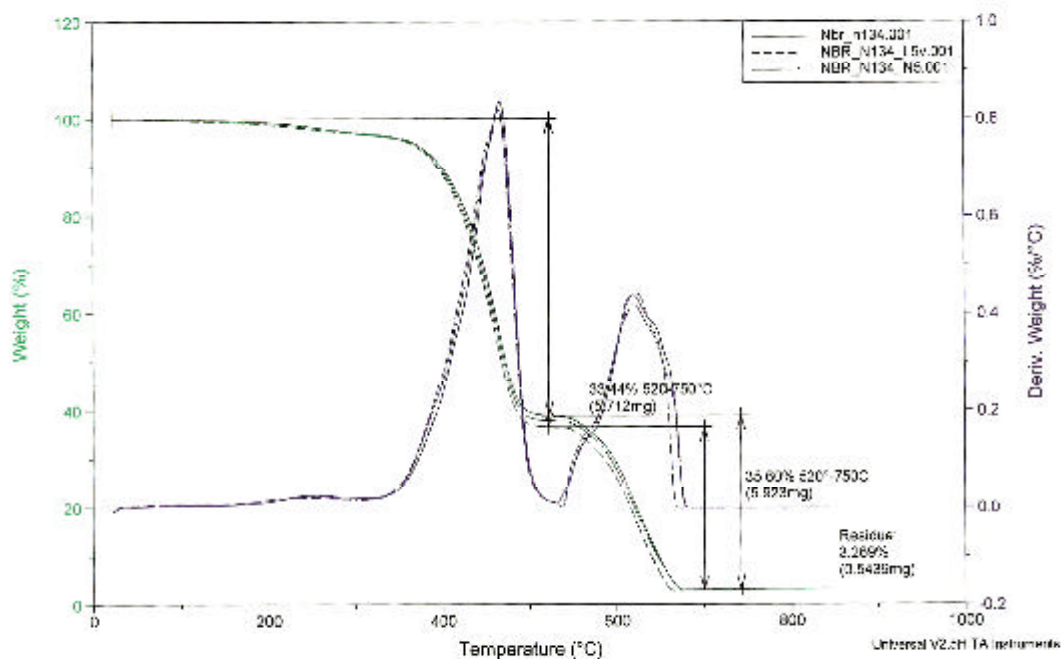


Fig.6. 5 TGA analysis to determine final CB content in the mixed compound

Effect of CB structure on CBS accelerated vulcanization:

As it has been presented, the effect of CB surface structure on the vulcanization reaction was studied by means of three experimental CB grades. As it can be seen in Table 6. 4 the main difference among them is the percentage of amorphous carbon present on their surfaces determined by Raman Spectroscopy. However, due to the changed parameters during production (reaction time) the surface of the CB containing higher ratio of amorphous carbon presents also a higher impurity level. Therefore, the vulcanization experiments were carried out both prior and after extraction (As explained in annex 1).

Table 6. 4 Characterization parameters for A1, A2 and A3

CB	Specific Surface Area m ² /g	% amophus C	Impurities (mg/g)
A1	118	11	15
A2	120	9	0.5
A3	121	7	0.5

6. INFLUENCE OF CB SURFACE ON VULCANIZATION AND RUBBER PROPERTIES

Fig.6. 6 and Fig.6. 7 show the SBR vulcanization curve at 30 and 50 phr respectively. In the present case The y axis does not present the torque but the percentage of vulcanization that is reached at a given time which helps to study the vulcanization kinetics. On the other hand, M_H-M_L values related to the final cross-link density are presented in Fig.6. 8.

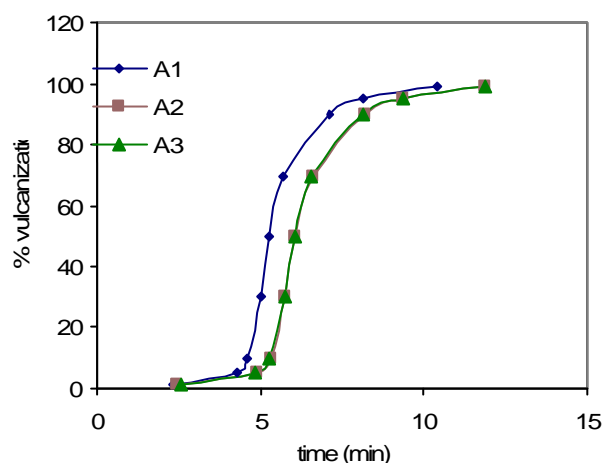


Fig.6. 6 Vulcanization reaction for CB at 30 phr

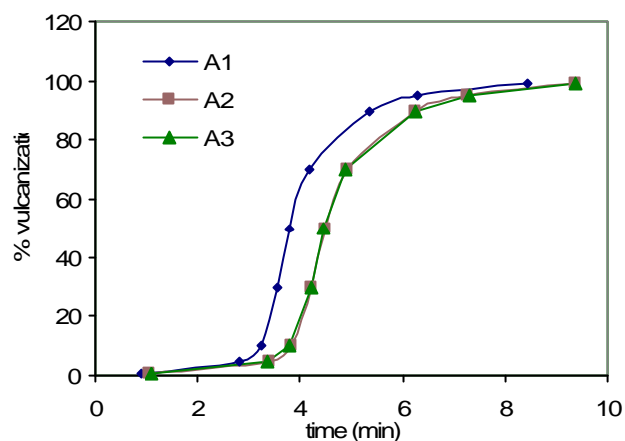


Fig.6. 7 Vulcanization reaction at 50 phr

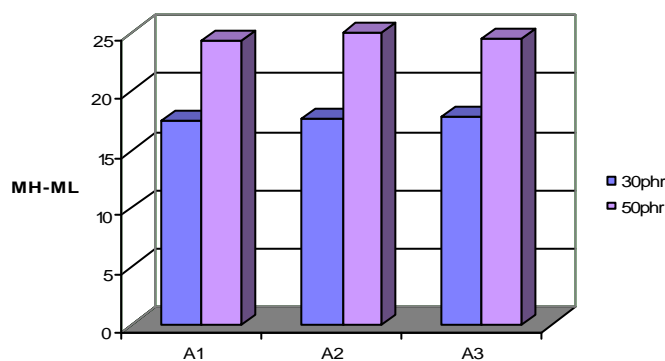


Fig.6. 8 M_H-M_L for both 30 and 50 phr filled SBR containing A1, A2 and A3

In the presented results several points are worth to comment. In the vulcanization curves the role of CB and its influence on vulcanization can be observed. It can be seen how increasing the CB amount from 30 to 50 phr does indeed accelerate the vulcanization reaction as the 100% vulcanization is achieved in much shorter times. On the other hand, increasing the CB amount also increases the value for the M_H-M_L which is an indication of a higher crosslink level, however, the presence of a higher CB loading also contributes to this phenomena and it is difficult to separate those two contributions.

6. INFLUENCE OF CB SURFACE ON VULCANIZATION AND RUBBER PROPERTIES

But much more interesting it is to observe the role played by the CB surface. As it can be seen in both cases, at 30 and 50 phr A1 (the one presenting higher amorphous content) presents a faster reaction kinetics, while M_H - M_L levels stay the same. This is a first indication that CB surface does contribute to the observed effects shown during the vulcanization reaction. However, as it has been presented in Table 6.4 A1 presents a large amount of tar on its surface. In order to know whether the presence of those species are responsible for the observed effects, A1 and A3 were extracted and the same experiments were again conducted. Results can be observed in the following figures.

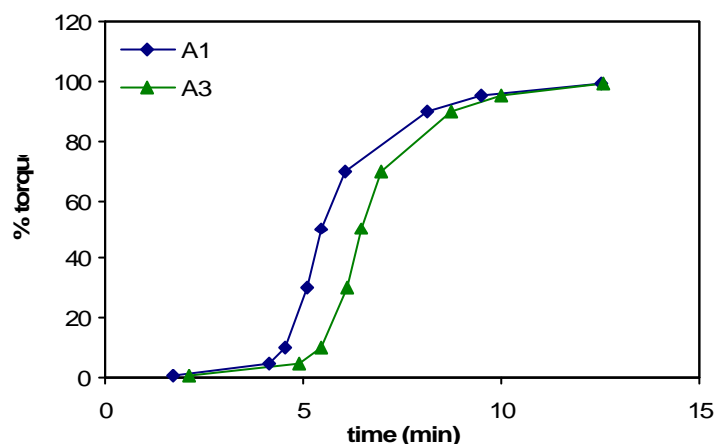


Fig.6. 10 Vulcanization reaction for 30 phr

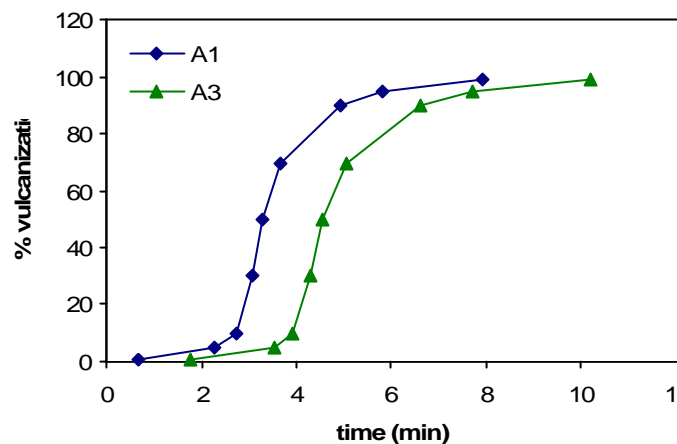


Fig.6. 9 Vulcanization reaction for 50 phr

The presented results show that no difference could be found before and after the extraction of CB concerning the vulcanization kinetics. The A1 extracted carbon still presented a much faster vulcanization reaction than the extracted A3. As far as M_H - M_L is concerned, values were the same for both type of CBs which means that no influence on the cross-linking level was present in the final compounds.

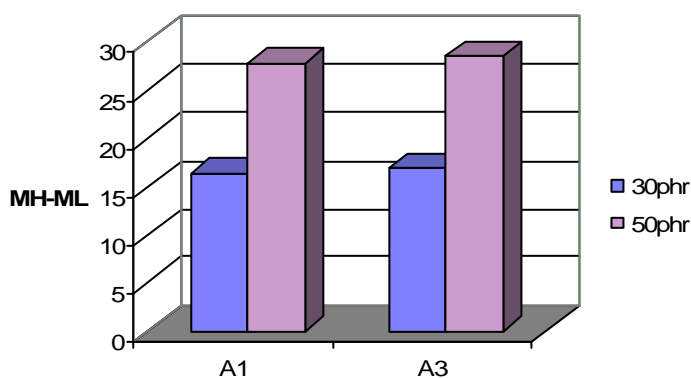


Fig.6. 11 MH-ML for Extracted A1 and A3 SBR compound

Changes produced in the vulcanization reaction by the APP modification of CB (air and nitrogen plasma) were also studied by means of the rheometric curves. In this case a compounds containing 50 phr of CB was mixed using polybutadiene rubber (BR) and nitrilebutadiene rubber high nitrile content (NBR). Because no changes were observed due to the presence of impurities on the CB the CB were used without prior extraction. The rheometer curves obtained both for the NBR and BR filled compounds are presented here (Fig.6. 12 and Fig.6. 13). Although the figures present only one of the curves, three different tests were carried out in order to obtain a mean value for each parameter. The values are presented in Table 6. 5.

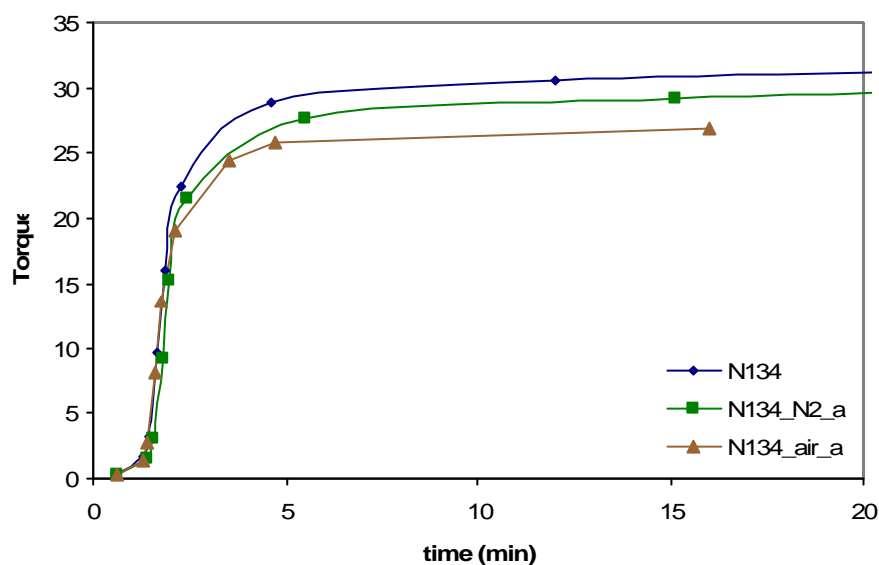


Fig.6. 12 Rheometer curves obtained for filled NBR (50phr)

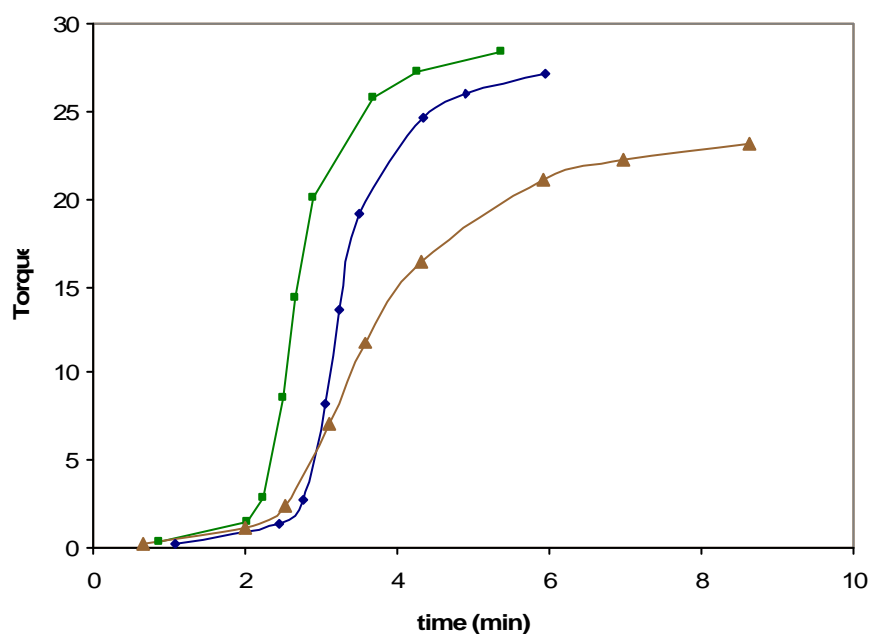


Fig.6. 13 Rheometer curves obtained for filled NBR (50phr)

6. INFLUENCE OF CB SURFACE ON VULCANIZATION AND RUBBER PROPERTIES

Table 6. 5 Obtained results for CB treated by APP

Polymer	NBR			BR		
	Air APP	N ₂ APP	Untreated	Air APP	N ₂ APP	Untreated
N134 CB grade						
M _H -M _L	25,36	28,12	29,45	18,43	25,27	24,5
M _L	1,83	2,22	2,41	4,99	3,39	2,9
T1(min)	0,61	0,63	0,64	0,65	0,87	1,05
T90 (min)	3,34	4,78	4,59	5,93	3,67	4,32
Shore-A	72	77,6	77,1	66,6	69	68,3

The presented results do not show much relevant changes in the case for NBR rubber. No changes were observed for the t_1 which indicates the beginning of the vulcanization reaction. However, it is possible to observe that for the air treated APP CB compound shorter t_{90} were obtained indicating that the vulcanization reaction is terminated earlier than for the two other CB's. If the final M_H-M_L was the same for all grades a shorter t_{90} would indicate that the same crosslinking level was achieved in a shorter period of time, but looking to the M_H-M_L levels it is possible to observe that air APP treated CB is lower than the others. Therefore, the shorter t_{90} does not indicate probably a faster reaction but a lower crosslinking level reached during vulcanization, but also could indicate a lower contribution of the CB network in the measured torque. The toughness measure presented in Table 6.5, indicating a lower Shore-A value for the air APP treated CB compound is also an indication that this type of CB influences the vulcanization reaction. Presentation of the results obtained for the BR rubber will probably help to clarify the phenomena.

In the case of BR vulcanization compounds, the differences are much significant. First of all in this case an evident change in t_1 is observed, much shorter values are observed for air APP treated CB compound followed by nitrogen APP treatment and finally the unmodified N134. On the other hand, t_{90} differ also between the three vulcanized samples. On one hand, air APP treated CB presents the longer t_{90} while the nitrogen APP CB is the faster achieving 90% of the vulcanization level. In this case M_H-M_L values are much lower for the air APP CB. Once again because the CB level is the same for all three compounds the most probable reason for such difference is a much lower crosslink density which is also indicated by a lower Shore_A toughness.

A possible hypothesis which will be further discussed by means of the MCV approach is here presented: It is known that CB may interact with the vulcanization chemicals such as the accelerating system, including sulphur and accelerators (CBS), it has been proposed that the interaction of CB with such chemicals may be the reason for a faster vulcanization kinetics when this filler is present. But it could also be that when the filler presents a high polarity (as is the case of the air APP treated CB) this species will be highly adsorbed on the CB surface and they are prevented from taking part in the vulcanization reaction. That should also explain why such a difference is observed between NBR and BR compounds. The higher NBR polarity due to its nitrile groups, prevents the CBS molecule from being highly absorbed on the CB surface as compatibility of this molecule with the polymer

matrix is enhanced. However, even in this case it is possible to observe a final slightly lower M_H-M_L , which could be related to a CBS permanent adsorption on CB. On the other hand, in the case of BR, the higher apolarity of this polymer promotes the migration of the CBS to the CB surface. The CBS-CB initial contact might be beneficial to start CBS decomposition and therefore to decrease t_1 as observed. However, if the adsorption becomes too strong the effect explained above will take place obtaining longer t_{90} and lower M_H-M_L values. As a conclusion it could be said that adjusting CB polarity to the polymer and the accelerant molecules (CBS) vulcanization rate and final crosslink could be optimized as is the case for nitrogen APP treated CB in BR compounds.

The effect of APP modification was confirmed by looking at the stress-strain curves for the BR vulcanized compounds which confirmed that better properties were obtained after nitrogen atmospheric plasma (Fig.6. 14). Air treated CB presented a curve which corresponded to a lower cross-link level as it has been already seen in the vulcanization curve. Therefore, the influence of CB in the vulcanization does not only affect the curing time but also the final properties of the compound which shows the importance to know more about the CB surface properties which may influence in the vulcanization reaction.

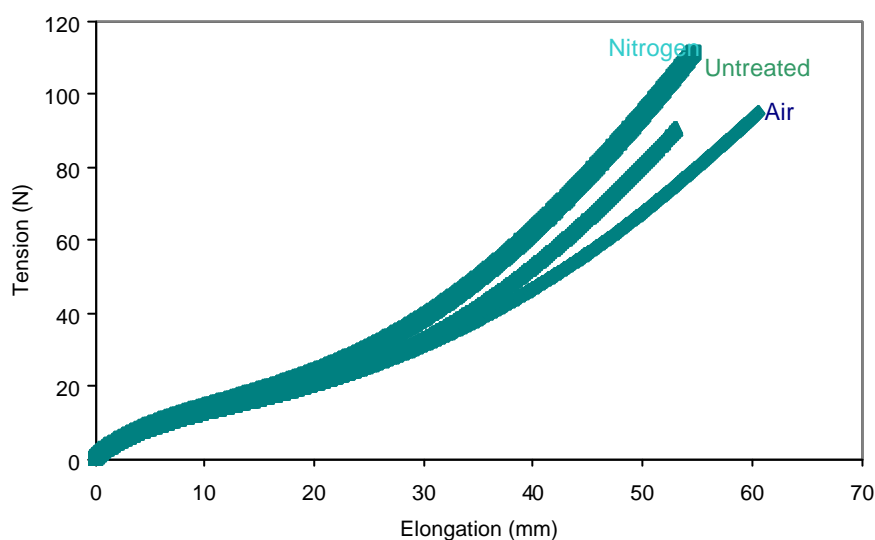


Fig.6. 14 Stress-Strain curve for the BR filled compounds

The above presented results by means of the rheometer curves were studied also using the MCV approach in order to understand in more detail the molecular process which lead to such macromolecular responses.

6.1.5 Results by MCV Approach:

The vulcanization reaction was studied by means of MVC vulcanization using the composition shown in Table 6. 6. As already said, the finality of this study is to find a possible explanation for the changes that have been already observed in the vulcanization reaction due to modification of CB surface nature. This technique allows to follow the accelerator decomposition and its intermediates formation along the vulcanization reaction and therefore, it can provide very interesting information about the mechanism which is followed in the presence of each CB.

Table 6. 6 Formulation for MCV experiments

Chemical	Amount (phr)
Squalene	100
CB	10
CBS	1.6
S ₈	2
ZnO	5
Stearic Acid	2

The species that were monitored during the reaction are presented in Fig.6. 15 where their evolution during the reaction is also shown. It is known that in order to start vulcanization the CBS molecule (Initial accelerator) must be decomposed to MBTS (accelerator intermediate) which will further react and give MBT as final vulcanization specie. It has also been shown that MBT may act as a catalyst for CBS decomposition, therefore, once the reaction starts reaction velocity increases (N. Agulló 1998)

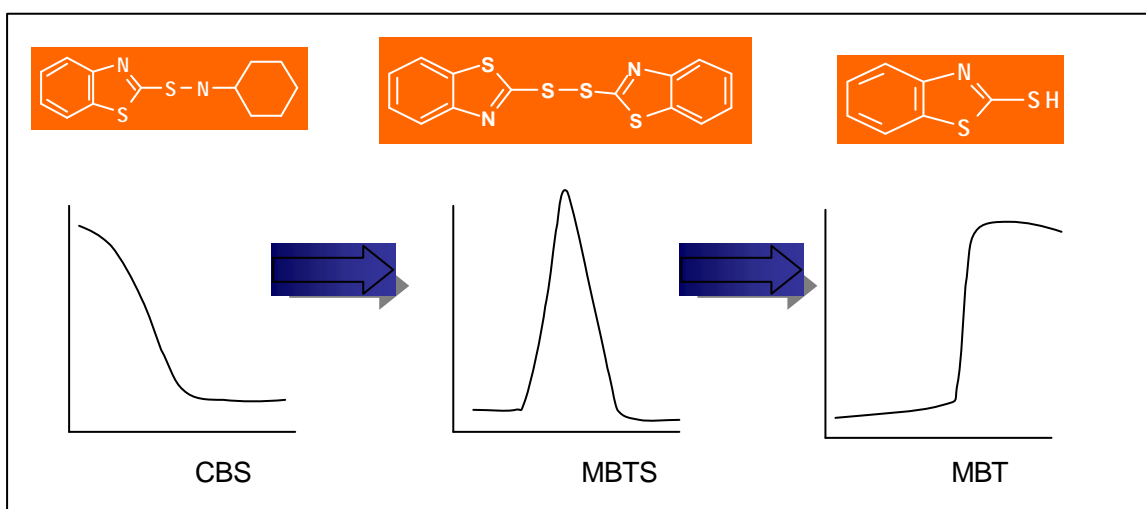


Fig.6. 15 Studied accelrator species and intermediated during the MCV reaction.

The mentioned accelerator species together with S_8 were followed during the vulcanization reaction at 140°C by quenching the reaction at several reaction times (from 0 to 50 min.). Although detailed information about the sample preparation and analysis can be found in [annex 7](#) a brief description is given here. Several vessels containing about 2.5 grams of the initial mixture were heated in a oil bath at 140°C and acetone- CO_2 bath was used to stop the reaction. The accelerator species were extracted by acetonitrile and analyzed by HPLC as shown in Fig.6. 16. Results are given as percentage of the total area detected in the chromatogram. Reproducibility of the sample preparation and species detection was already studied in previous works of our research group.

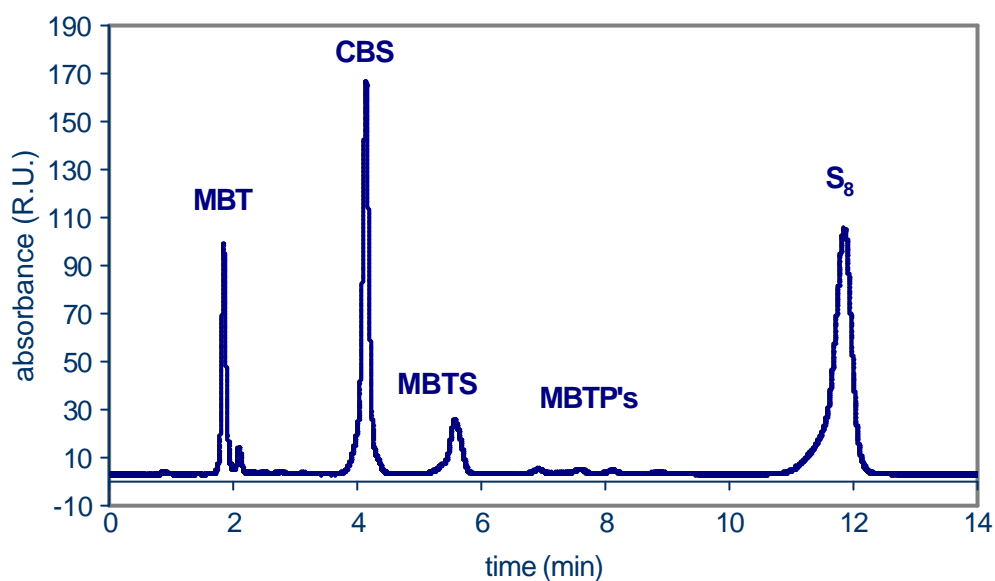


Fig.6. 16 HPLC chromatogram showing the separation of the accelerant species and S_8

Influence of CB Structure on the Vulcanization reaction:

As first result the effect of CB N134 on the decomposition of CBS is presented in front of a formulation containing no CB. It was also thought that it would be very interesting to observe the effect of N134g, in order to study whether all type of C surface had the same effect or if other parameters such as C structure was also relevant. As it can be seen in Fig.6. 17 the presence of CB does increase the velocity of CBS decomposition being completely depleted after 15 minutes reaction time. However, this is not the case neither for the non-containing CB formulation nor for the N134g. The results show that not only the presence of CB is important for the vulcanization kinetics but also the nature of such carbon surface.

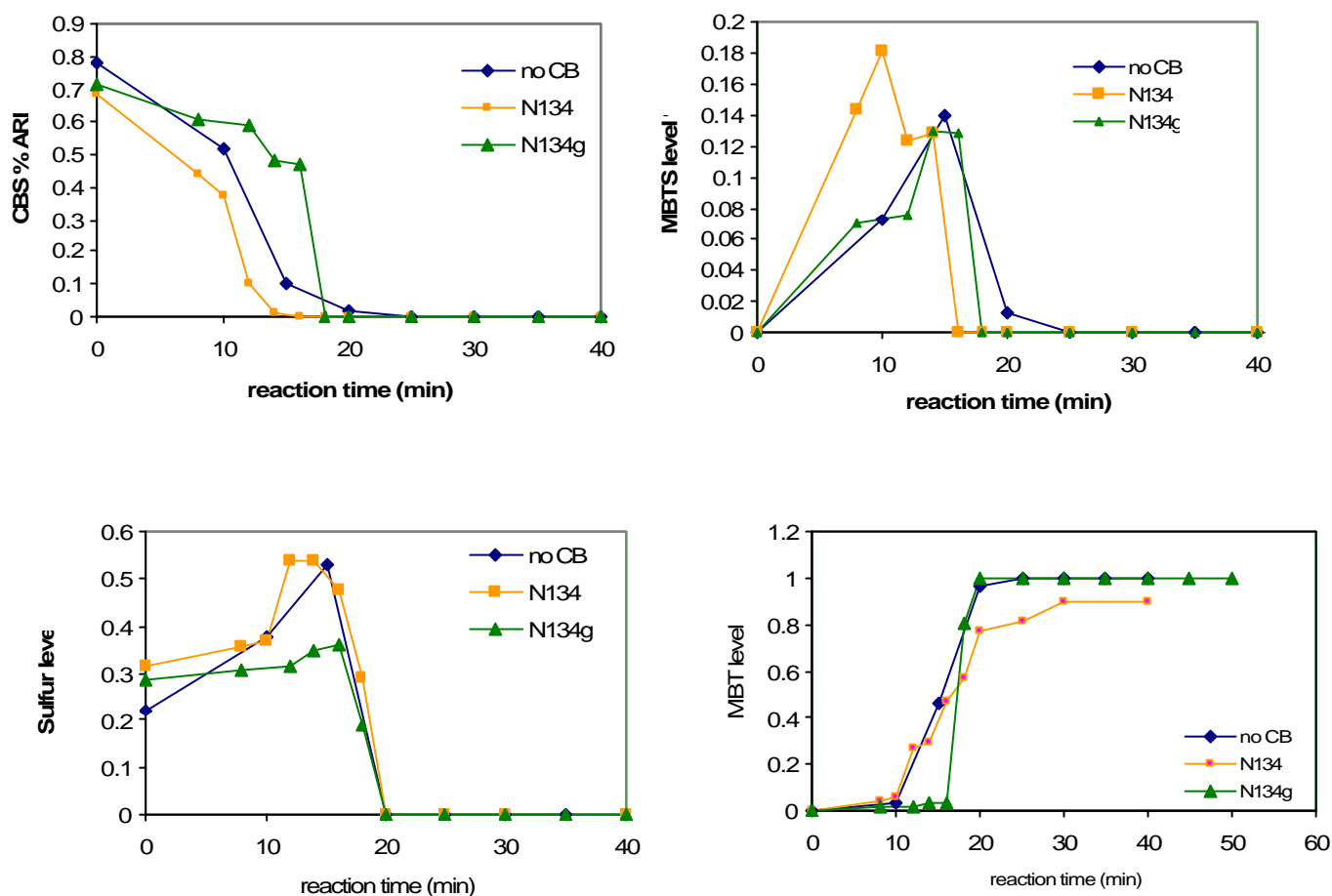
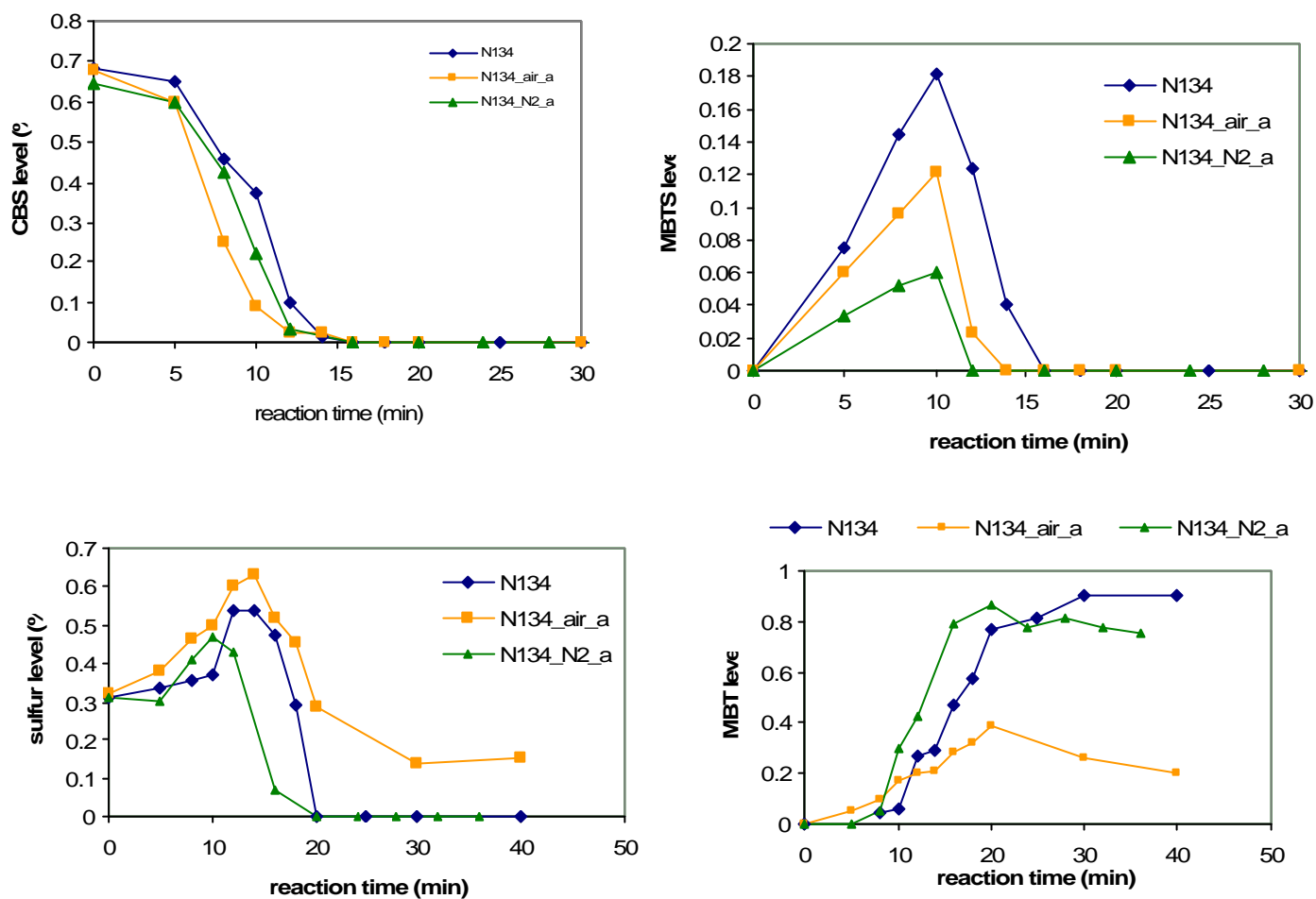


Fig.6. 17 CBS, MBTS; MBT and Sulphur decomposition for unfilled, N134 and N134g formulation

As it can be observed in the figure above, CBS decomposes faster in the presence of N134 than without CB or N134g. Consequently, MBTS intermediates are formed earlier. However, MBT is not the only final specie for this reaction as is the case for N134g and without CB, were relative are becomes equal to the MBT area. This might be an indication that other species are formed during the reaction. These phenomena will be studied in more detail.

Influence of APP treated CB in the vulcanization reaction:

Because filled rubber with APP modified CB's vulcanization was studied by means of the rheometric curves and some interesting changes were found as presented, the same CB's were also studied by means of the MCV approach in order to try to find more information about the changes produced in the vulcanization reaction. The evolution of the accelerator species is presented here.



As it can be seen in the figure above, the CBS decomposition, which has to take place before starting the vulcanization reaction and which is responsible for the scorch time, changes for the plasma modified carbons. Both oxygen and nitrogen APP treated carbons reach the total decomposition of CBS before the unmodified CB. It can be concluded then that the plasma modification helps to decompose the accelerant, and which is even more important that there is an interaction between the CB surface and the accelerant. Whether it is just a physical adsorption or if it chemically reacts is more difficult to state, however the figures corresponding to the other species can give us important information. It is worth to remember that the same effect was observed when vulcanizing BR compounds which is coherent as squalene can also be considered an apolar media more similar to BR than to NBR.

As it can be observed from figure showing MBT levels, the final product after CBS decomposition and vulcanization reaction, the level for the air APP modified CB is much lower. A possible explanation for this effect is that the reaction path for the vulcanization reaction is altered by the presence of such a filler. For nitrogen APP treated CB the MBT is formed faster than for the other two CB grades. As a matter of fact the MBT curves are

also consistent with the observed results for the BR vulcanization. In those curves air and nitrogen APP CB presented also shorter t_i but while N_2 APP compound increased fast and steeply the torque, air APP's increase was slow and lower.

The hypothesis of a change of mechanism during crosslinking is also confirmed when following the intermediate sulfur level during the reaction, which also indicates the absence of crosslinking reaction. Even when the reaction is considered to be finished and all the accelerant (CBS) is decomposed (after 30min. of reaction) There is still a high level of sulfur that has not been introduced in the chains for the formulation containing N134_air_a.

It was also observed that during the reaction another unidentified peak which was very small for the other reactions and not taken into account, increased when using the air APP treated carbon during the MCV. The new peak appeared at a retention time of 1,544min. instead of 1,304 min. corresponding to MBT. In this case we suppose that the low levels of MBT are due to the presence of this new final product. The evolution of this peak is shown at Fig.6. 19 for the different MCV's reactions. A previous study helped to identify this compound as mercaptiobenzotiazole (MTBT) (N. Agulló 1998).

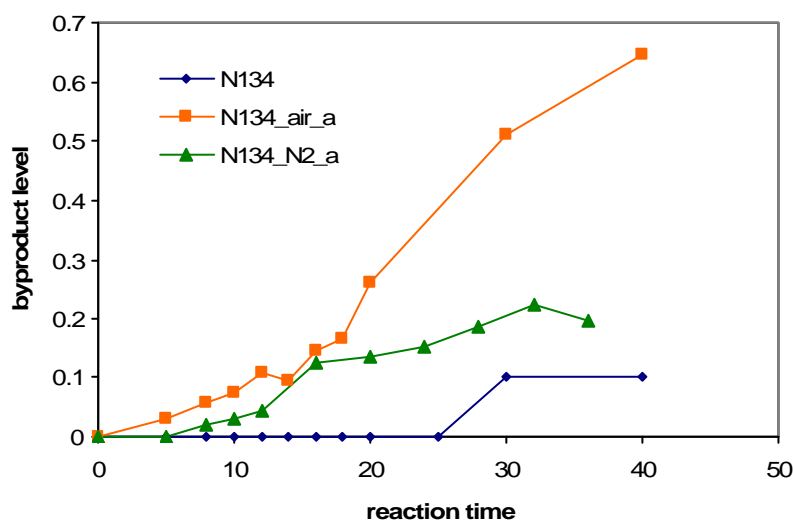


Fig.6. 19 MTBT evolution during MCV experiments

In order to corroborate that the oxygen species created during air APP plasma are the ones responsible for the mechanism change during the CBS decomposition reaction, a last experiment was performed. N134_air_a was treated with NH_3 LPP plasma in order to make the acidic groups react with the reactive plasma species as shown in chapter 5. The MCV reaction was carried out using such modified CB. Results are shown in next figure.

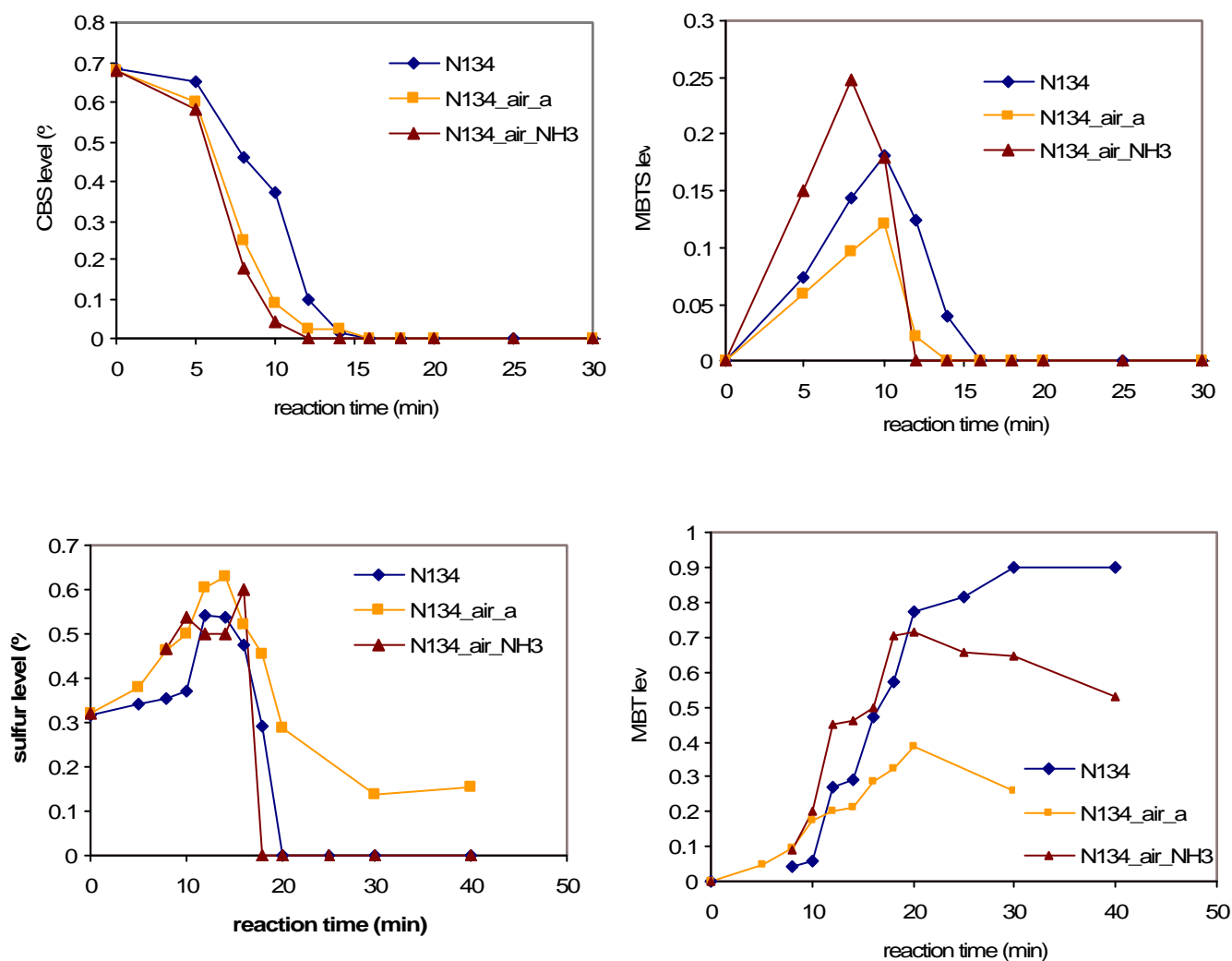


Fig.6. 20 CBS, MBTS; MBT and Sulphur decomposition for unfilled, N134 and N134_air_a and N134_air_NH₃

In the results shown in the figure above it can be seen that even after the ammonia LPP treatment the N134_air_a still decomposes CBS faster than regular unmodified N134. However, in this case of sulfur it can be observed how already after 18 minutes there is no more sulphur left in the formulation which indicates that have been used to cross-link the molecules. It seems therefore that the presence of the oxygen groups is needed in order to catalyze the MTBT formation which prevents vulcanization. This is confirmed when looking at the MBT formation. It is possible to observe that higher MBT levels than for N134_air_a are obtained for N134_air_NH₃ indicating that although some changes are still present the reaction path may be more similar to that of the original N134.

To conclude this experiment the level of the new final product (MTBT) was also observed to be lower after the LPP NH_3 modification. This fact leads to the conclusion that the oxidized groups formed on the CB surface during the air_APP treatment are the ones responsible for changing the CBS decomposition path leading to an unreactive cross-linking specie (MTBT). On the other hand when polarity of the CB is increased without the presence of such oxidized groups the reaction is faster without involving such mechanistic changes.

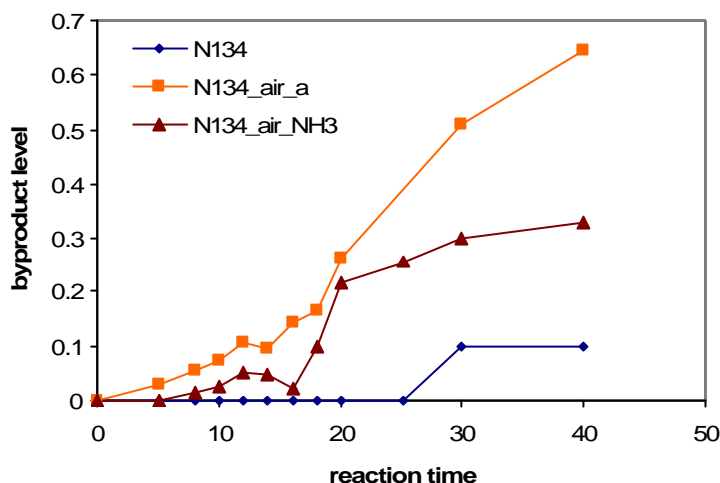


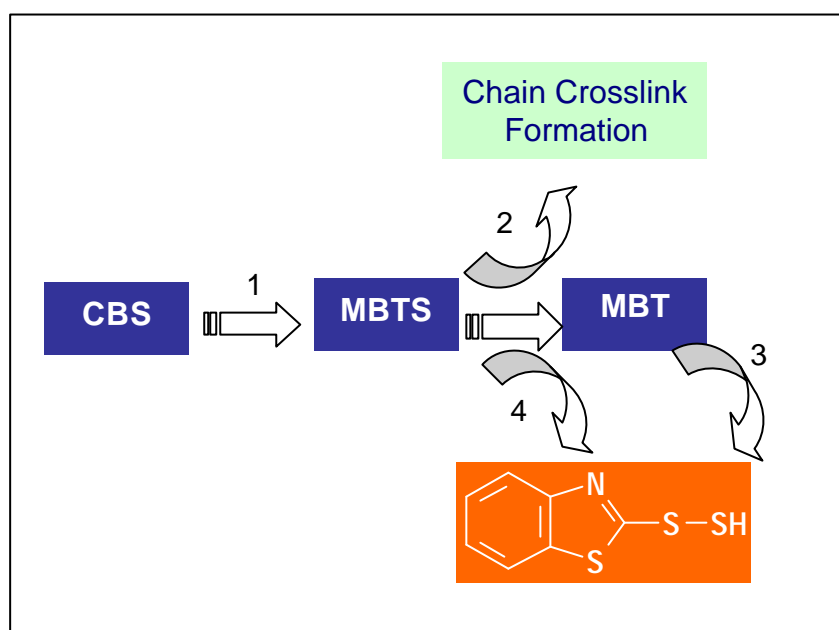
Fig.6. 21 Evolution of the new final accelerant product MTBT

6.1.6. Discussion of CB role on Vulcanization reaction

Both rheometer studies and MCV have contributed to study the effect of CB surface during the vulcanization reaction. Both techniques confirmed that the presence of amorphous carbon on the surface of CB leads to a faster reaction rate without severe modifications on the final cross-link level. A faster decomposition of the accelerant (CBS) on the surface of CB containing such amorphous structure is a very likely reason to be responsible for such changes.

On the other hand changes produced during APP treatment have helped to understand already described effects such as lower crosslink densities and lower vulcanization rate when vulcanizing NR in the presence of oxidized CB (Cotten 1979). Although faster CBS decomposition was observed in the presence of both air and nitrogen APP treated CB's the vulcanization mechanism has been shown to be altered by the N134_air_a CB. However, in order for this change to take place, CBS must be adsorbed on the surface of CB which only happens when the polarity difference between the filler and the rubber is high enough. This is the reason why such effects were not observed during NBR (high nitrile content) vulcanization.

Adsorption and presence of high oxidized groups on the CB surface is necessary in order to obtain MTBT during the vulcanization reaction which prevents sulfur to go into the crosslink reaction staying in the formulation. However, this specie was also shown to appear at long reaction times for N134. The appearance of such molecule could be due to a final reaction of MBT with some lousy bounded Sulfur of a polysulfuric bound between two squalene or polymer chains which could help to provoke reversion. On the other hand if such reaction takes place before the sulfur forms part of sulfur bounds between the chains it will never get there as the case of vulcanized BR in the presence of N134_air_a. A scheme of the process taking into account MTBT formation is presented in the figure below:



- 1- CBS decomposition to MBTS
- 2- MBTS introduction to the polymer chain to form sulfur bridges by S_8 inclusion
- 3- Finally decomposition of MBTS to MBT which leaves the sulfur bridge as cross-link
- 4- Possible post-reaction of MBT with lousy bonded long sulfur bridges to form non-crosslinks
- 5- Direct reaction of MBTS to form (MTBT) which does not allow sulfur to form part of the cross-link bridges.

However, as it has already been explained, CBS must be found on the CB surface so that the phenomena explained in this section takes place. The adsorption of chemicals used for rubber compounds such as antioxidants and other stabilizers has already been described. An increase in CB surface polarity, probably due to a HNO_3 oxidation, increased the adsorption of polar molecules such as benzoic acid, phenol or propanol (J.M. Peña et al. 2001a, 2001b, 2001c and A.P. D'Silva 1998). Because CBS is also a rather polar molecule similar behaviour could be attributed.

In order to study this adsorption process the following experiment was set up. 40ml of a solution containing 300ppm CBS in squalene are prepared and a variable amount of CB is added into each vessel (0,2 g, 0,6 g, 1,0 g, 1,4 g, 1,8 g, 2,2 g). The samples were left overnight in an orbital stirrer in order to reach the adsorption equilibrium. After this period the solution is filtered through a 45 micron nylon filter and 0,1g of the clean solution are weighted for each sample. Acetonitrile is used, as for the MCV reaction, in order to remove the unadsorbed CBS which is quantified by means of HPLC using a calibration curve shown in Fig.6. 23.

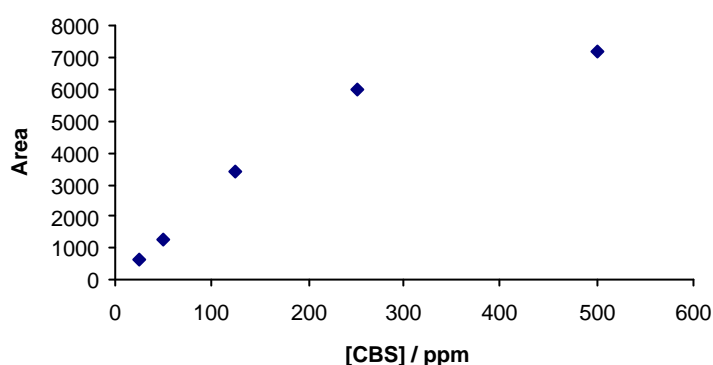


Fig.6. 22 CBS detection by HPLC, linear range determination

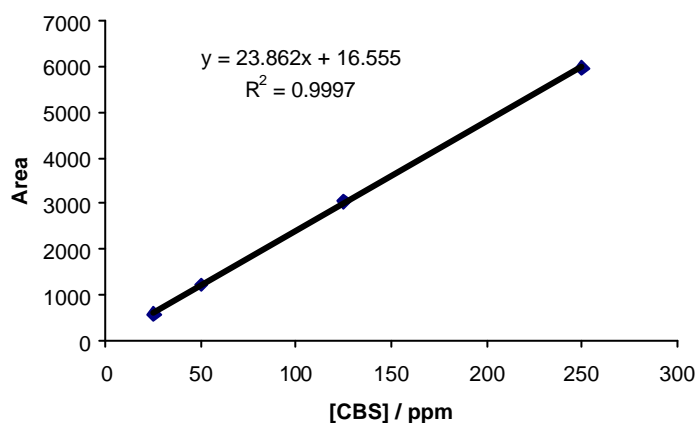


Fig.6. 23 CBS calibration curve used to determine adsorption on CB

As it is shown in Fig.6. 22 linear for CBS detector is maintained up to 300 ppm, the figure below shows the calibration curve used in order to calculate the CBS which is not adsorbed on the surface of CB. The amount of adsorbed CBS as a function of CB amount was plotted as shown in Fig.6. 24 The slope obtained from the fitted line was taken as a measure of the adsorption capacity of a given CB.

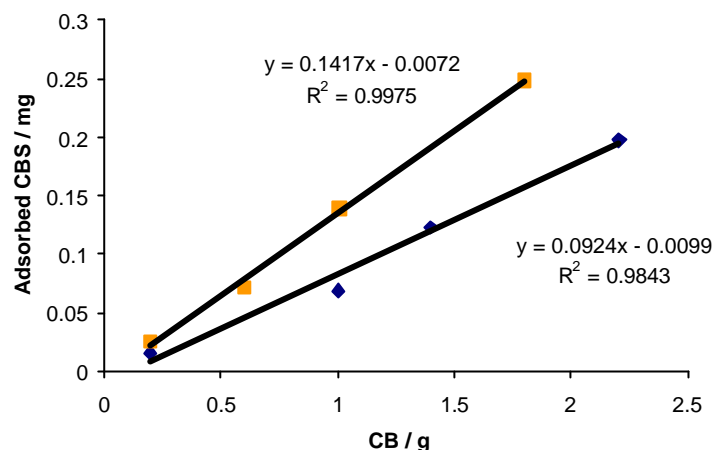


Fig.6. 24 Adsorption capacity determination for 2 CBs

In order to study the adsorption behavior on CB several treatments were carried out on the CB surface. CB was treated using the down-stream LPP reactor in Acrylic Acid (AA) and Methylmethacrylate (MM) as shown in table in order to change the surface polarity.

Table 6. 7 Modification in LPP reactor to study the effect on CBS adsorption

Monomer	Power (W)	Time (min)
AA	20	20
AA	20	40
AA	20	60
AA	40	20
AA	60	20
AA	80	20
MM	20	10
MM	20	20
MM	20	40
MM	20	20
MM	40	20
MM	80	20

Fig.6. 25 presents the adsorption plot for the AA-LPP modified carbon at different generator powers. As it can be seen unmodified carbon seem to loose linearity earlier than modified CB's which is already a sign of the increase in the adsorption capacity for those modified carbons.

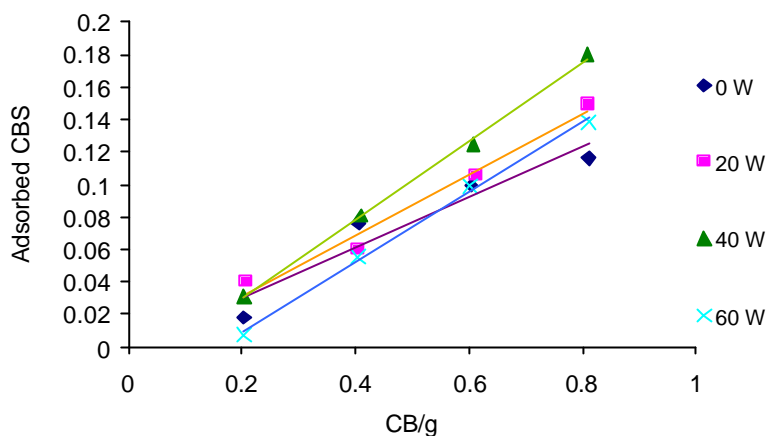


Fig.6. 25 CBS adsorption from esqualene solution for AA- LPP modified CB (effect of generator power)

Next figure presents the adsorption capacity of the presented blacks in Fig.6. 26. As it can be clearly observed it seems that a maximum is obtained for 40 W treatment. This effect could be related to a maximum retention of the AA structure and a higher polarity of the carbon at the end of the LPP treatment.

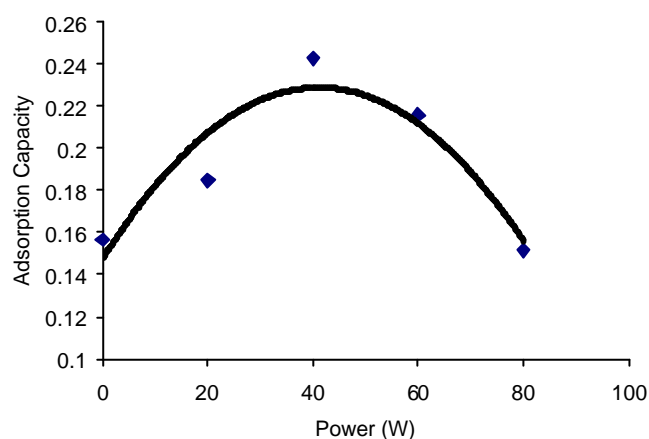


Fig.6. 26 Effect of the AA-LPP generator power on the CB adsorption capacity of CBS

When the effect of the treatment length is taken into account a similar effect is observed obtaining a maximum adsorption capacity at 20 minutes for a 20W AA treatment.

Table 6. 8 Adsoption capacity for AA-LPP treated CB's effect of treatment duration

Power(W)	Time (min)	Slope (adsorption capacity)
0	0	0,0915
20	20	0,2072
20	60	0,1742

In the case of the MM modified CBs the effect of the treatment is much more homogeneous. Being a much apolar molecule the adsorption although also high is higher than for unmodified carbon but almost no difference is observed when changing the Power of the LPP generator.

Table 6. 9 Effect of generator power on the adsorption capacity of MM modified CB

Power (W)	Time (min)	Adsorption capacity
0	0	0,0915
20	20	0,1853
40	20	0,1865

As a conclusion of the presented results it can be said that adsorption of the vulcanization accelerator (CBS) on the CB may be modified by changing the polarity of the CB surface as shown during AA-LPP modification. Further studies involving desorption process as for example in a Soxhlet extraction could help to determine whether the adsorption process is reversible and to which extent in each case.

6.2 Polymer Filler Interaction

So far the influence of CB in the vulcanization reaction and the effect produced by the plasma treatments has been presented. However, vulcanization is not the only parameter which may influence the final properties of the material. Filler polymer interaction, which starts to develop during the mixing process of the polymer with the filler, is also known to play a key role in order to obtain a high performance compound. Although several methods in order to evaluate this phenomenon have been described two of them will be here presented: bound rubber and polymer adsorption from solution.

6.2.1 Bound Rubber

Bound rubber has been known since 1925 and is considered as a measure of rubber-to-filler interaction. Since filler-polymer interaction has a major influence on the composite's flow properties, the study of this phenomenon becomes essential. Bound rubber is determined as the rubber portion that can not be separated from the filler when the filled compound is extracted in a good polymer solvent, such as toluene, during a certain period of time. The larger the amount of polymer that stays on the CB, the better the polymer-filler interaction which has also been related to improved final properties.

The interactions that keep the polymer on the CB surface preventing the rubber from being dissolved in the solvent can be explained from two different views:

- On one hand, bound rubber has been regarded to be caused merely by adsorption effects in which Van der Waals forces and chemisorption play the main role. (G. Kraus, 1971).
- On the other hand, bound rubber formation has been attributed to a chemical process. This process was assumed to be caused by reactions of the rubber with functional groups or aromatic hydrogen present on the surface of CB, (D.Rivin, 1971). Also the reaction of rubber radicals formed by mechanical-chemical degradation during mixing with active sites newly formed on carbon black, for example due to the breakdown of its structure during mixing (J.B. Donnet and E. Papier, 1972).

In contrast to the old days, today, there is the general agreement among most experts that although covalent bonds between rubber and CB surface contribute to rubber reinforcement, they are not an indispensable prerequisite for bound rubber formation and rubber reinforcement. For example, it is perfectly known that bound rubber level decreases when temperature is increased. When the extraction temperature is related to the bond energy it can be confirmed that only 20% of bound rubber can be attributed to covalent bonds between rubber and CB (A.K. Sicar and A. Voet, 1970). Among the adsorption processes, physical adsorption has been found the most likely to occur as bound rubber tends to zero when the extraction process is performed above 80°C, (M.J Wang et. al., 1993). Low resolution proton NMR studies have also evidenced the presence of physical adsorption in the polymer-filler interphase (V.J. McBrierty and J.C. Kenny, 1994).

Different CB parameters have been found to be related with bound rubber level, and consequently to filler-polymer interaction, such as specific surface area or CB structure and surface activity (S. Wolff et al.1993, J.L. Leblanc and P. Hardy, 1991, W.H. Hess et al., 1973, W. Wang et al., 1994)

CB surface treatments, such as polymeric grafting (J.-B. Donnet et al., 1989), or γ radiation (F. Cataldo, 2001), which cause surface activity changes have also been reported to affect the filler-rubber interaction, as well as some oxidation processes on CB for which bound rubber was described to observe when mixed with polar polymers such epoxydized Natural Rubber (ref)

Besides the effect of CB characteristic parameters and polymer nature, the sequence of adding ingredients has also been found to be another critical parameter that influences bound rubber determination. There is a good reason why CB mixed in the presence of other ingredients gives lower bound rubber levels than with polymer alone (J. Leblanc and P. Hardy, 1991). When CB is mixed with other ingredients, the amount of available surface area and the available number of filler active sites for polymer adsorption can be notoriously reduced by the adsorption of these molecules

on the CB surface. Once the ingredient molecules have been adsorbed, it is very difficult to replace them with polymer chains. During mixing, the more polar ingredients which have a poorer compatibility with low polar polymers, will be driven to the filler surface where the polarity is relatively higher. It is obvious to think that the higher the difference between polymer and filler polarities the higher amount of ingredients will be adsorbed on the filler surface. Once again, filler surface energy and more specifically its polar component is related to the polymer-filler interaction.

In concluding, bound rubber can play an important role in efficiently slowing the flocculation rate of filler aggregates by increasing polymer matrix viscosity, increasing the effective dimension of aggregates and fixing the filler-polymer complex by crosslinking the polymer shell with the polymer matrix. As a result a number of structure-properties relations have been established between the content of bound rubber and the mechanical properties of filled rubbers (E. M. Dannenberg, 1986). Other studies have related the bound rubber level with the scorch time reduction effect produced by the presence of fillers during vulcanization (B. Sohn and Ch. Park, 1996).

6.2.2. Polymer Adsorption from Solution

Another way to study the interaction between CB and the polymer chain is by means of adsorption of polymer chains in solution on CB. Although this method is less used than the bound rubber presented above it can be very helpful to study more in detail the adsorption process on the surface of CB. The polymer adsorption from solution was first described a long time ago, when it was observed that polymer adsorption took place from polymer solution reaching an apparent adsorption value with increasing polymer concentration (J. Hobden et al 1953, G. Kraus et al. 1955).

Since that time many studies on this field have helped to better understand polymer adsorption on CB. It has been shown that although low weight polymer molecules would be adsorbed faster, they are later replaced by higher weight polymer molecules (G. Kraus et al. 1968, P. Patat 1966). It was also shown that the solvent may also affect the process as higher adsorption was observed for bad polymer solvents (D. Busmann 1992).

The effect of the adsorption temperature has also been evaluated for polyisoprene dissolved in cyclohexane where it was observed that no changes were observed in a temperature range from 25 to 60°C. In the same study the influence of the CB specific surface area was examined and the results found show that increasing specific surface area increases polymer adsorption as expected, however when the specific surface area is larger than approximately 120m²/g a decrease in the adsorption capacity was observed. This effect was attributed to the filler agglomeration which tends to be higher in the small particle size CB due to a higher surface energy and a smaller interparticle distance. It is

worth to mention that the lost of linearity between the adsorption capacity and the specific surface is dependent on the type of adsorbed polymer (D. Busmann 1992).

6.2.3. Bound Rubber Results

Bound rubber was studied in this work for several compounds in order to study the polymer-filler interaction. The compounds that have been studied are presented in Table 6. 10.

Table 6. 10 Used Compounds for Bound Rubber determination

CB grade	CB phr	Polymer
N134	50	BR
N134_air_a	50	BR
N134_N ₂ _a	50	BR
N134_(N ₂ +NH ₃)_a (0.5L/h)	50	BR
N134_(N ₂ +NH ₃)_a (2L/h)	50	BR
N134	50	EPDM
N134_(N ₂ +NH ₃)_a (2L/h)	50	EPDM

In the present case bound rubber experiments were conducted for a week. A piece of 0,2 g of rubber was cut in small pieces (3mm x 3mm approximately), placed in a glass 50 ml. flask with cap. They were shaken in an orbital stirrer for a week. Each two days the solvent was carefully changed. In some cases experiments were done at high temperature, for this purpose round flasks with water cooler were utilized. Bound rubber levels were calculated by weight difference.

Two main different tests were carried out, on one side, the effect of APP treatment both with air and nitrogen plasma on the interaction between CB and. Four different conditions were studied which are shown in Fig.6. 27. Bound Rubber was determined at 23°C, at 80°C but also after heating the compound at 150°C (to simulate vulcanization temperature) and finally after introducing CBS and the other vulcanization chemicals (sulfur, ZnO, stearic acid) in the compound to observe the effect of this ingredient on the polymer-filler interaction.

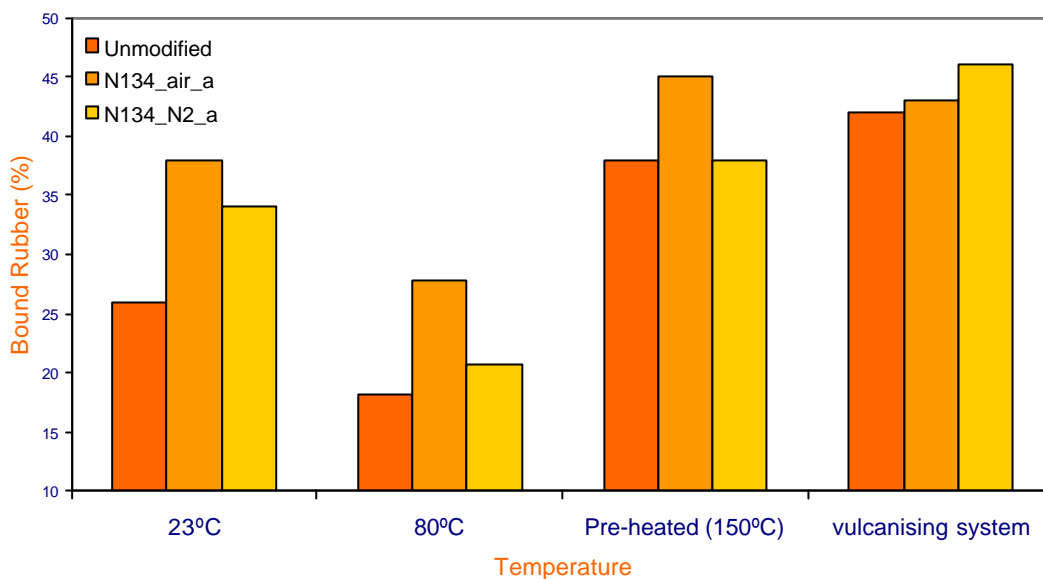


Fig.6. 27 Bound Rubber level for BR filled compounds at several conditions

As it can be seen in the figure above, bound rubber at 23°C was increased for both APP treatments both with air and nitrogen being slightly higher for the air treated CB N134. Both the acidic groups present on the surface but also new exposed surface due to the “cleaning effect” attributed to this type of treatment could be the reason for this increase in the polymer filler interaction. On the other hand, as described already in literature, measurements at higher temperatures (80°C), decrease the filler-polymer interaction. It is important to notice that despite the decrease the value remain higher for the APP treated CB samples. This effect is an indication that different type of polymer-filler interaction takes place in the compounds which is stronger than the interaction developed by untreated CB surface.

For the rubber samples which were placed at 150°C overnight, the bound rubber level increases, in this case it is possible to observe that the compounds containing unmodified N134 and the one containing nitrogen APP treated samples have the same bound rubber value. The bound rubber level for the air treated sample stays still higher which indicates some type of polymer-filler interaction which does not exist in the other two cases.

Last condition including the vulcanizing system in the mixture does present higher levels than for measurements at room temperature. This can be due to a low degree of vulcanization which will preferably start at the surface of CB. But it is also very interesting to notice in this case that air plasma treated CB presents almost the same level than untreated CB, while the sample containing nitrogen APP treated CB is the one presenting higher levels. This result indicate that bound rubber is affected by the presence of the vulcanizing system in the mixture, as species may be adsorbed on the CB surface as shown in the results presented in the previous section. Moreover it is here observed that

vulcanizing system and probably CBS trend to adsorb more on the high polar air APP treated sample decreasing its Bound rubber level when compared to the nitrogen APP treated CB. This result is in perfect agreement with the results obtained during the vulcanization studies where a very strong interaction between the CBS and the surface of N134_air_a treated carbon was shown. The interaction was so powerful that it even changed the vulcanization mechanism leading to poorer final properties.

Therefore, although bound rubber may be an indication of polymer filler interaction, it may not be hundred percent true when comparing CB's with different surface and adsorptive properties in the absence of the vulcanization system.

Bound rubber measurements were also used in order to study the filler-polymer interaction between BR and Ethylene-propylene-diene-monomer rubber (EPDM), after CB modification in APP using nitrogen as plasma gas and ammonia as post-treatment. Fig. 6. 28 shows the bound rubber measurements which were done after 1 3 and 6 days. In the cases where CB was suspended in the solution, TGA measurements instead weight differences were done in order to obtain the polymer amount adsorbed on the CB (mainly for EPDM compounds).

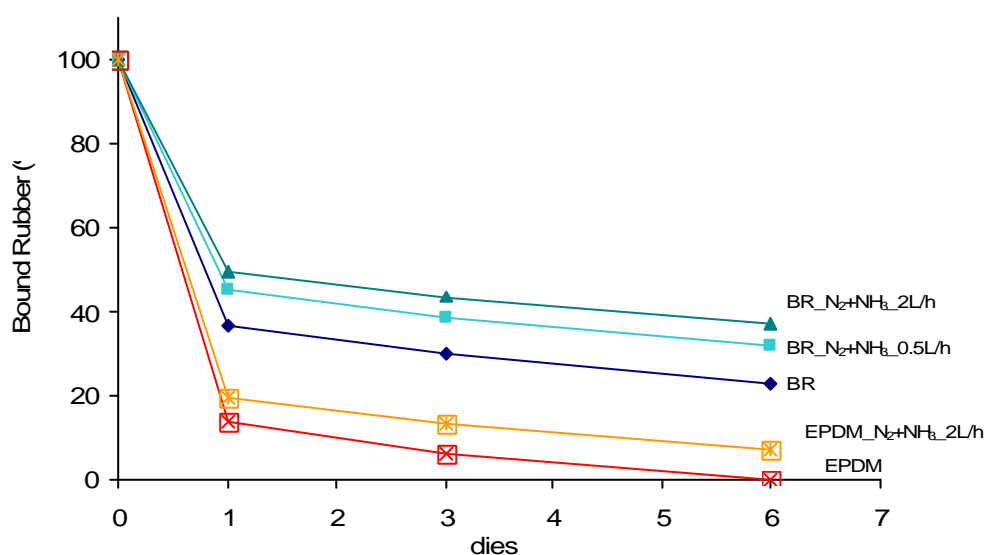


Fig.6. 28 Bound rubber for N134_N₂+NH₃_a CB in BR and EPDM compounds

As it

can be seen in the figure above all the CB grades treated with the NH₂+NH₃ combination present higher bound rubber level than for the original CB. It can also be observed that bound rubber decreased steeply during the first 24 hours.

For the BR filled bound rubber measurements it can be observed that the bound rubber increased with increasing ammonia flow into the system. In the case for EPDM filled with unmodified CB almost no polymer could be detected by TGA after 6 days of extraction but still 10% bound rubber could be detected if the N134 was modified by means of APP

nitrogen and ammonia plasma. This is quite an unexpected result as the plasma treatment is expected to increase the polar part of the energy of the filler. However, as it has been earlier shown in the previous chapter (Ch. 5.5.), in the case of XPB 171 atmospheric plasma treatment the surface energy was overall decreased. This surface energy decrease could help to improve CB dispersion and improvement of the filler-polymer interaction. On the other hand ammonia containing plasmas have already been presented as very mild systems to introduce polar groups but they do affect surface final composition which might also help to improve the adsorption.

6.2.4. Polymer Adsorption from Solution Results

Polymer adsorption from solution was carried out following the methodology described by D. Busmann which is here presented briefly (D. Busmann 1992). 0,4 g. of CB were left for 1 day in suspension in 40 ml. of polymer solution at different concentrations (between 0,5 and 4 g/L). After separating the CB by means of a centrifuge, the unadsorbed polymer was determined by weight of a known volume after drying the solvent at 100°C for 3 hours.

Polymer adsorption was studied on both APP treated CB on BR and EPDM solutions. Polymers were the same than the ones used to prepare the compounds previously studied.

As it is observed in Fig.6. 29, BR adsorption was modified by the APP treatment performed on N134. The trend is the same as observed for Bound rubber experiments confirming all previous results. Air APP modified CB presents a higher adsorption capacity on its surface followed by the nitrogen

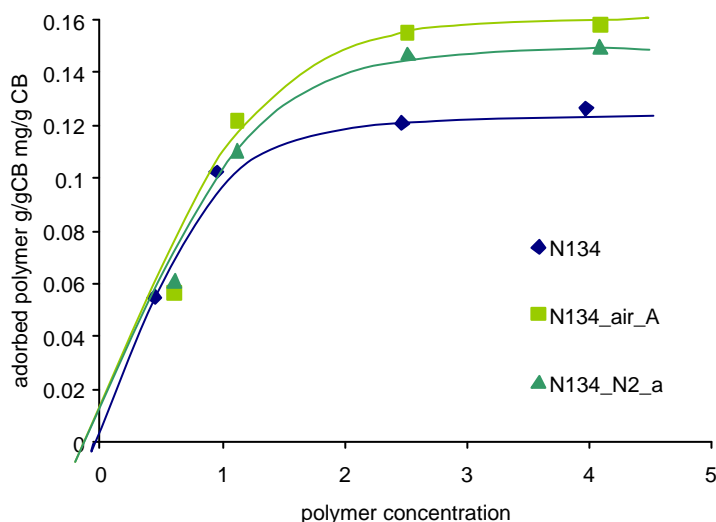


Fig.6. 29 BR Adsorption from solution of N134 before and after APP treatment

It would be very interesting to study in more detail the same adsorption experiments including the presence of CB in the adsorption media which would probably compete with the polymer molecules. Unmodified CB presented the lowest adsorption capacity. Whether these changes are related to the surface chemistry modification shown in chapter 5.4, or maybe related to a possible change in the CB surface structure as shown by XRD is difficult to assess, but it is possible to observe that modification in the very first layers of CB composition do affect the final behavior of such material.

Last figure shows the adsorption behavior for EPDM in the same conditions than for BR presented experiments. Contrary to the previous case, it is possible to see how for low polymer concentrations (1g/L up to 3g/L) adsorption behavior is decreased for the APP treated samples. As a matter of fact the order is just opposite to the one for BR, obtaining a higher adsorption for unmodified N134, followed by nitrogen APP treated carbon and finally the air APP treated CB. However, it can also be observed that the higher the polymer concentration the shorter the gap in the adsorption level for such fillers. This could be because at low concentrations the polymer chains (very apolar in this case) are strongly repelled from the carbon surface which agrees with the polarity and adsorption capacity of the fillers. However, for high polymer concentrations this effect is diminished, once some polymers are attached to the CB surface it is easier for the others to adsorb.

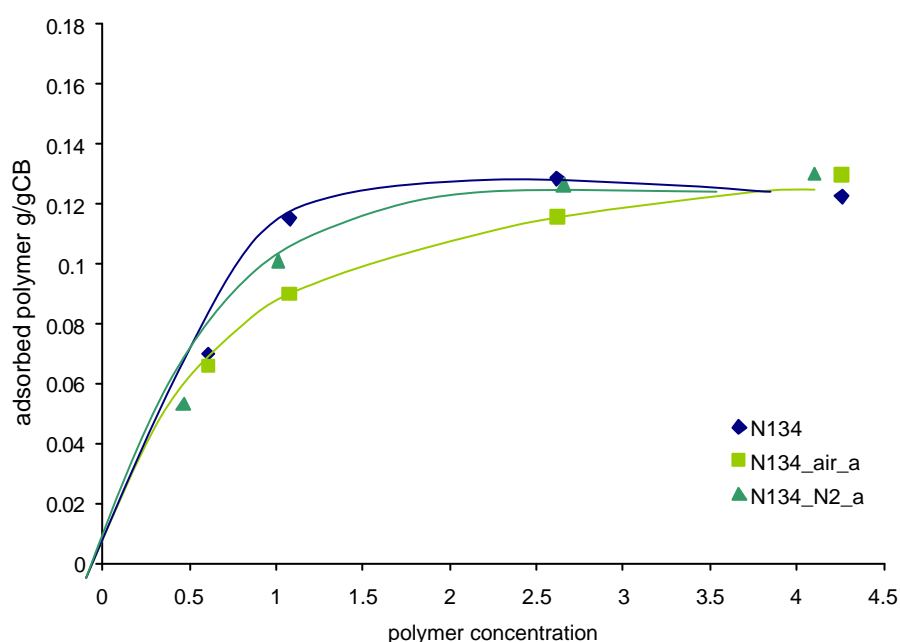


Fig.6. 30 EPDM Adsorption from solution of N134 before and after APP treatment

As a conclusion of the presented results in the filler-polymer interaction section it can be stated that changing the very first layers of CB surface, (without modifying other key parameters such as specific surface area), it is possible to modify the interaction of CB and the polymer chains. APP treatments have turned to be a good technique to

accomplish this task. However, the adsorption of other molecules in the compound has to be taken into account as they can enter in competition with long polymer chains as showed in the bound rubber experiments.

Finally, as a conclusion of this chapter it can be said that APP treated CB's which had been previously characterized have 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 relevance 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 does catalyze the CBS decomposition but at the same time changes the reaction mechanism due to MTBT early formation. On the other hand nitrogen APP treated CB obtains a faster CBS decomposition without changing the final product of the reaction. Adsorption of CBS on the CB surface is necessary in order to accelerate such reaction.

It has also been seen that the surface changes also altered the polymer-filler interaction both by BR and polymer adsorption from solution but sever care has to be given to the presence of other compounds that may compete for such adsorption positions.

REFERENCES:

- N. Agulló, Study of the sulfenamide and sulfenamide thiuram accelerated system for natural rubber vulcanization using the modelling approach, Doctoral Thesis Institut químic de Sarrià-Universitat Ramón Llull 1998
- J. A. Ayala, w. M hess, G. A joyce, f. D. Kistler, carbon black-elastomer interaction: ii: effects of carbon black surface activity and loading rubber chemistry and technology 66 (1993) 772
- J. A ayala, w. M hess, f. D. Kistler, g. A joyce, carbon-black-elastomer interaction. Rubber Chemistry and Technology 64 (1991) 19.
- J.J. Brennan and d.h. Lambert rubber-black, interaction influence on the cure level of vulcanizates, rubber chemistry and technology 45 (1972) 94
- D. Busmann russ-kautschuk wechselwirkungen, dissertation deutsches institut für kautschuktechnologie, Hannover, Deutschland 1992
- F. Cataldo, fullerene-like structures as interaction sites between carbon black and rubber, Macromolecular symposia 228 (2005) 91
- R. Cotten, effects of carbon black surface properties and structure rheometer cure behavior. Rubber chemistry and technology 45 (1972) 129
- G. 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 (1979) 477
- M. Gessler, evidence for chemical interaction in carbon and polymer associations. Butyl and acidic oxy blacks. The possible role of carboxylic acid groups on the black, Rubber chemistry and technology 42 (1969) 850
- G. Kraus, J.T. Gruver, Molecular weight effects in adsorption of rubbers on carbon black. Rubber chemistry and technology 41 (1968) 1256
- E. Morita, correlation analysis of curing agents, rubber chemistry and technology 57 (1984) 744
- E. Morita and A. Sullivan, Thioketals as prevulcanization inhibitors, rubber chemistry and technology 51 (1983) 1132
- J. L. Leblanc and p. Hardy evolution of bound rubber during storage of uncured compounds Kautschuk Gummi and Kunststoffe 44 (1991) 1120

6. INFLUENCE OF CB SURFACE ON VULCANIZATION AND RUBBER PROPERTIES

- S. J. Park, M.K. Seo and Ch. Nah, influence of surface characteristics of carbon blacks on cure and mechanical behaviors of rubber matrix compounds journal of colloid and interface science 291 (2005) 229
- S.J. Park, J.S. Kim, surface energy characterization of modified carbon blacks and its relationship to composites tearing properties. Journal of adhesion science and technology), 15 (2001) 1443
- D. Patterson, J Koenig, J. Shelton , vulcanization studies of elastomers using solid-state carbon-13 NMR , rubber chemistry and technology 56 (1983) 971
- J.M. Peña, n.s. Allen, m. Edge and c.m. Liauw, factors affecting the adsorption of stabilizers on to carbon black (flow micro-calorimetry studies), dyes and pigments 49 (2001a) 29
- J.M. Peña, n.s. Allen, m. Edge and c.m. Liauw, factors affecting the adsorption of stabilizers on to carbon black (flow micro-calorimetry studies) part ii: hindered amine light stabilizers, journal of materials science 36 (2001b) 4419
- J.m. Peña, n.s. Allen, m. Edge and c.m. Liauw, factors affecting the adsorption of stabilizers on to carbon black (flow micro-calorimetry studies) part iii: surface activity study using acid/base model probes, journal of materials science 36 (2001c) 4433
- F. Patat, e. Killmann, c. Schliebener, adsorption of macromolecules from solution rct 39(1966)36
- M. Porter, t. D. Skinner, m. A. Wheelans, structural characterization of vulcanizates. Part viii. The n-cyclohexylbenzothiazole-2-sulfenamide-accelerated sulfur vulcanization of natural rubber at 140-180°C. And of synthetic cis-1,4-polyisoprene at 140°C, Journal of applied polymer science 11 (1967) 2271
- A.K. Sircar and A Voet, immobilization of elastomers at the carbon black particle surface, rubber chemistry and technology 43 (1970) 973
- P. D'Silva, adsorption of antioxidants by carbon blacks, carbon 36 (1998) 1317
- J. H. M. Van den Berg, J. Beulen, J. M. H. Hacking, e. F. J. Duynstee, Model vulcanization of epdm compounds? Part ii: influence of temperature and time on the vulcanization products from ethylidene norbornane , rubber chemistry and technology 57 (1984) 725
- D. Rivin, j. Aron and A.I. Medalia, Bonding to carbon black by sulphur vulcanization rubber chemistry and technology 47 (1968) 330

6. INFLUENCE OF CB SURFACE ON VULCANIZATION AND RUBBER PROPERTIES

- F. Messiner, bound rubber theory and experiment, journal of polymer applied science 50 (1993) 285
- S. Wolff, M.J. Wang, E.H. Tan, Surface energy of fillers and its effect on rubber reinforcement. Part 1. Kautschuk Gummi kunststoffe 47 (1994) 780
- S Wolff, M. J.wang, e. H tan surface energy of fillers and its effect on rubber reinforcement. Part 2. Kautschuk gummi kunststoffe 47 (1994) 873