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The role of carbon black surface activity and specific surface area in the vulcanization reaction

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Activitat superficial vesus superfície específica en la reacció de vulcanització.

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RESUMEN

Se sabe que es importante la interacción polímero-carga para obtener materiales de caucho de buen rendimiento. Sin embargo, cómo puede afectar la presencia del producto de relleno en el proceso de curado y en los mecanismos por los cuales el negro de humo y el polímero interactúan, es algo que no se ha descrito en su totalidad en los estudios realizados hasta la fecha. Cada día es más habitual considerar los compuestos poliméricos como dos redes o cadenas interpenetradas. Desde este punto de vista, es preciso que se desarrollen algunas técnicas para estudiar la formación de la red de negro de humo y las variables que pueden influir en este proceso. Respecto a la reacción de vulcanización, existen algunos resultados contradictorios, pero la influencia de la presencia del negro de humo parece ser clara. El papel de la superficie específica y de la actividad superficial del negro de carbono se discuten en este artículo. La posibilidad de adaptar estas propiedades para obtener una mejor cohesión entre las dos redes interpenetradas y, como resultado de ello, artículos de mayor calidad, es el motivo del porqué no sólo los grupos de investigación de polímeros sino también la industria del caucho puede estar interesada en este tema.

Palabras clave: Negro de humo. Actividad superficial. Vulcanización del caucho.

SUMMARY

This paper reviews the work developed in studying how Carbon Black presence may affect the vulcanization process and the mechanisms by which CB and polymer interact, which has not been completely described in the studies performed to date. The approach of considering polymer composites as two interpenetrated networks is reviewed. From this point of view, some techniques for studying the CB network formation and the variables that may influence this process are described, and the need to develop new ones is emphasized. Concerning the vulcanization reaction some contradictory results have been reported but the influence of the CB presence seems to be clear. The role of CB specific surface area and surface activity are discussed in this paper. The possibility of tailoring these properties in order to obtain better cohesion between the two interpenetrated networks and, as a result, higher quality articles is outlined.

Key words: Carbon black. Surface activity. Specific surface. Rubber. Vulcanization.

RESUM

Aquest article presenta el treball realitzat en l'estudi de la influència del negre de carboni en la reacció de vulcanització. Així mateix, els mecanismes pels quals el negre de carboni i el polímer interaccionen. Es comenta la consideració dels materials polimèrics compostos com dues xarxes interpenetrades. Des d'aquest punt de vista, es descriuen algunes tècniques per a estudiar la formació de la xarxa de negre de carboni i les variables que poden influir en aquest procés. Es fa èmfasi en la necessitat de desenvolupar de noves. Respecte a la reacció de vulcanització, existeixen alguns resultats contradictoris, però la influència de la presència del negre de carboni sembla clara. El paper de la superfície específica i de l'activitat superficial del negre de carboni es discuteixen en aquest article. La possibilitat de dissenyar a mida aquestes propietats per a obtenir una major interacció entre les dues xarxes interpenetrades i, com a resultat articles de millor qualitat, ha fet incrementar l'interès d'aquesta línia de recerca.

Mots clau: Negre de carboni. Activitat superficial. Superfície específica. Cautxú. Vulcanització.

INTRODUCTION

In order to obtain elastomeric composites with good featuring properties, polymer chains must be cross-linked each other. One of the most important processes used in the rubber industry to achieve this result is sulfur vulcanization. Activators and accelerators are needed to obtain a reasonable reaction kinetics and effectiveness while the presence of fillers in the vulcanized compound, especially CB, is required to obtain suitable mechanical properties. This vulcanization process may take place following different chemical paths, which have been found to be strongly dependent on the vulcanization system⁽¹⁻⁵⁾. However, it is not only the curing agents that can alter the reaction mechanism; the presence of fillers can also modify some of the

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steps involved in this process⁽⁶⁾. For instance, the use of CB has been shown to decrease the scorch time and to act as a catalyzer of the cross-link formation. It has also been published that CB can absorb the accelerators' intermediates on its surface making the formation of sulfur bridges between the chains on the filler-polymer interphase easier⁽⁷⁾. Moreover a higher monosulfidic bridge content has been reported for polymeric mixtures containing this type of filler^(8,9). From the structural point of view different energy level sites have been reported to exist on the CB surface. The presence of these sites confirms the approach of describing the CB surface as a two-phase structure that combines semi-crystalline domains with so called amorphous carbon. These two different regions can be detected and studied by Raman Spectroscopy. Specially high activity has been found in the union of these two well-differentiated regions⁽¹⁰⁾. It is worth pointing out that although the interaction between the polymeric and the filler phase is known to be important, the interaction mechanisms are still not well explained. Therefore, the filler influence in the vulcanization reaction and final properties of the vulcanizate is an interesting issue for many research groups in the field of polymers, and as a result, the understanding of filled polymeric materials as a composite of two different networks, the polymer on one hand and the CB on the other, has become more common in the last few years⁽¹¹⁻¹³⁾. To make this possible, many techniques have been developed to evaluate the properties and behavior of both phases, and to help to find out the parameters that play a significant role during the formation and of course, in the performance of the final material. This paper aims to give a brief overview of some of these techniques and their results, especially those that are focused on describing the influence of CB surface activity and its specific surface area. No doubt, these two properties can be used to characterize CB but there are still many others that need to be studied to fill some of the remaining gaps in this polymer-filler interaction phenomenon.

CB SURFACE

Since the use of CB as filler for polymer formulations was discovered, there have been many attempts to characterize this material. Its specific surface area, structure and conductivity among others, are still today some of the parameters used to describe the different CB grades due to the relationship found between them and some of the macromolecular properties required in rubber articles^(14,15).

Another interesting parameter, although more difficult to understand and describe, is CB surface activity. We will focus on two of the techniques that have been used to study and measure this property.

Maurer described a way of measuring this activity as the temperature at which 15% of CB is decomposed during a thermogravimetric analysis⁽¹⁶⁾. Following this procedure a good correlation between specific surface area of CB (measured as a nitrogen adsorption isotherm) and the surface activity was found. This result leads to the hypothesis of considering that all CB grades have the same surface activity per unit of area, which means that active sites are the same for all CB. However, some exceptions to this trend have been found when some special CB grades such as Durex-0 from Degussa or surface treated regular CB grades were analyzed (figure 1). These deviations could only be explained if their surface activity was influenced by some other effects such as higher activity sites located on their surface⁽¹⁷⁾.

Another way to study the surface activity is by Inverse Gas Chromatography. To perform the experiments the column is filled with CB, which is previously sieved to select a pro-

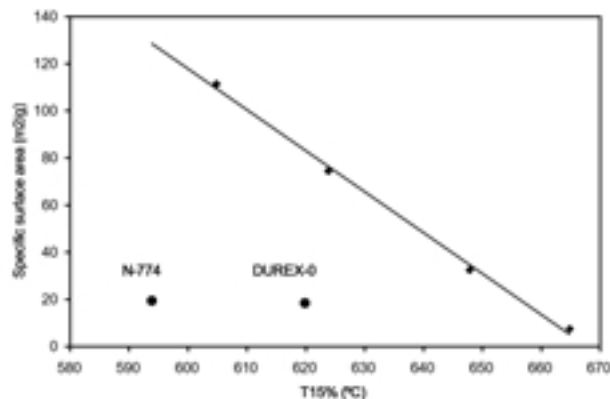


Figure 1. Some special CB grades have deviations from Maurer's correlation.

per particle size, and the interaction with different molecules is studied at infinite dilution⁽¹⁸⁻²¹⁾. The particle size can be rather critical as CB grades with high specific surface area (higher than 100 m²/g) have a strong tendency to absorb the probes on their surface making it very difficult to obtain an infinite dilution analysis. The interactions that take place between the filler and the injected probes may have a different chemical nature; in order to explain surface activity more accurately two different components have been described. The dispersive component, which is due to weak intermolecular forces such as London dipoles, is measured using alkane probes while for the specific component caused by more electrostatic interactions polar probes are injected (figure 2). A linear relation between the dispersive component and the nitrogen absorption specific area similar to Maurer correlation has also been published in studies using this technique⁽²²⁾. On the other hand the specific component was also found to be dependent on the CB formation process and therefore some other factors such as the chemical surface composition or its morphological structure. These two components together are used to calculate the experimental absorption free energy giving this parameter a physical sense that could help to understand the polymer-filler interaction⁽²³⁻²⁵⁾. When the previous special CB mentioned above were used to fill the column an unusual higher polar component was found. In some cases the dispersive component due to London inte-

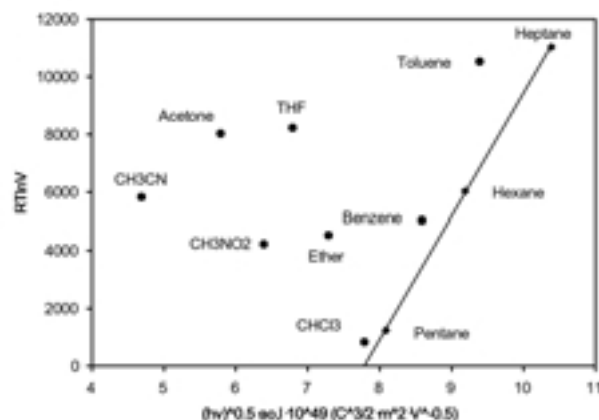


Figure 2. Dispersive probes (n-alkanes) have a linear correlation against many physico-chemical parameters. Specific probes also allow the elucidation of CB surface active points.

reactions was also above the expected value. Later in this paper we will describe how these two CBs also modify the decomposition kinetics of the CBS used as accelerator in the curing reaction. These results not only confirm the hypothesis of the presence of different energy sites on the filler surface but also that they could have different origins⁽²⁶⁾.

Moreover some other methodologies to describe the energy distribution of the CB surface have already been published. Schuster et al. have used an ethene isotherm to relate the carbon structure with its energy heterogeneity. Four different active sites were identified with the help of CB graphitized samples. From lower to higher energy sites described on the surface filler there are graphitic planes, amorphous carbon, crystallite edges and cavities. In the same paper it was also stated that the percentage of high energy sites is not constant for all CB grades and therefore the value of the specific nitrogen area is not sufficient to describe the filler surface activity⁽²⁷⁾.

CB production process and the feed stock origin have also been found to have an influence on surface activity. For thermal blacks obtained from oil feedstock an increase of surface activity has been observed compared to the same grade natural gas feedstock carbon blacks. The increase was explained by a reaction that takes place on the CB surface during its formation. Upon heat treatment, oxygen and sulfur groups are removed, creating vacancies. Some of these sites are "healed" by saturation with carbon atoms but others turn out to give very active sites for rubber reinforcement.⁽²⁸⁾

CB DISPERSION

The polymer-filler interaction starts when the formulation components (polymer, curing agents and fillers) are introduced in the mixer to obtain a homogenous material that will be cured later. To obtain a good filler dispersion the polymer and the filler need to have some affinity with each other. Several techniques have been used to elucidate the CB conductive network structure; this is an important aspect as the majority of rubber compound properties are related to the degree of CB dispersion. Some of the experimental tools that have been used for measuring dispersion are Transmission Electron Microscope, Mechanical Scanning Microscope, Optical Microscopy, and Reflectometry⁽²⁹⁻³³⁾. However, not all the techniques can give the same information, as the dispersion problem is a length scale phenomenon. Besides some of them require really complicated sample preparation and manipulation. One of the most powerful methods that have been described in the literature is based on electrical measurements^(12, 34, 35). This approach can study the dispersion down to the aggregate level as it allows evaluating the average gap between CB aggregates. Obviously dispersion will depend on the CB loading. Studies about this trend have led to the foundation of the percolation theory that postulates that when a sufficient amount of CB to form a continuous network is present in the polymer matrix, the resistivity decreases steeply. This network formation is very important for some of the material properties such as low strain viscoelastic properties⁽¹³⁾, when the strain increases the network is broken forming discontinuous sub-networks. The CB concentration in which this event takes place is known as percolation point and is clearly a function of the CB specific surface area. The higher the specific surface area, the easier it is for the filler to build a conductive network, but also the surface activity seems to play a significant role in the dispersion process. When studying the dispersion for CB with a high surface activity once again a deviation is observed also confirming the importance of the polymer-filler interaction during the mixing process (figure 3).

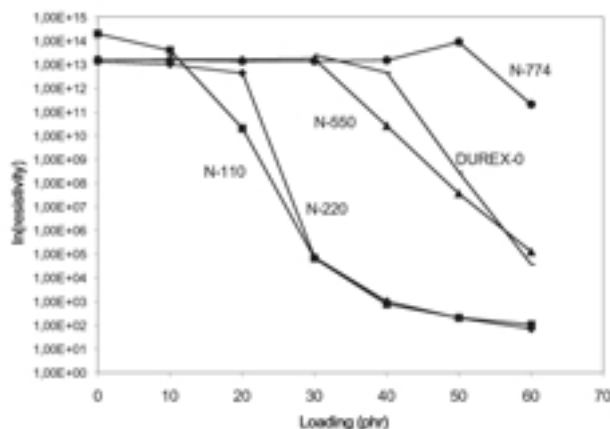


Figure 3. The electrical measurements allow to determine the CB loading when the complete network is formed. Although this concentration is specific surface dependent, surface activity also plays an important role.

Another way to study the filler dispersion and interaction with the polymer in unvulcanized compounds is to determine the bound rubber⁽³⁶⁻³⁸⁾. This procedure consists of evaluating the amount of polymer that remains attached to the filler network when a filled compound is extracted with an organic solvent. The chains that are not absorbed on the filler surface or those whose energy interaction is not high enough, are dissolved by the solvent. By weighing the sample before and after the experiment it is possible to calculate the bound rubber percentage. As could be imagined this value is polymer dependent having for instance higher levels for NR than for SBR. When CB has been treated thermally the amount of bound rubber decreases as the active sites become less frequent due to the growth of crystallites⁽³⁹⁾. Other variables to take into account are the filler loading and its specific surface area. At the same loading level CB grades with higher specific surface area obtain a higher bound rubber value as they offer a higher polymer-filler interphase where the interaction might take place. On the other hand the percolation effect can also be observed by this method. When the network has not yet been formed the amount of exposed surface increases linearly and as a result the bound rubber follows the same

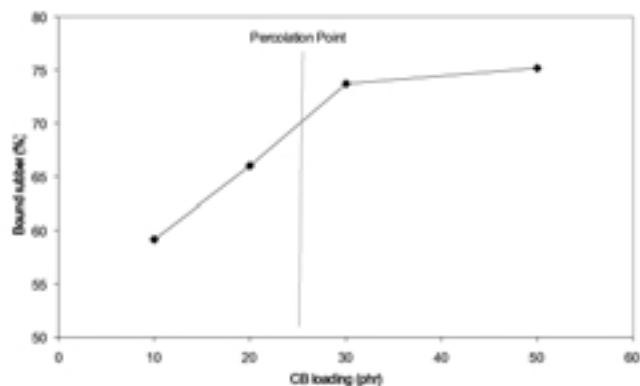


Figure 4. Bound rubber measurements are also affected by the CB aggregation as it can be seen over percolation point (25 phr).

trend. Once the network is completed the level tends to stabilize. A possible explanation could be that above the percolation point CB particles do not expose their whole surface to the polymer phase due to the interaction with other CB particles (figure 4).

THE VULCANIZATION REACTION

For many years although the cross-linking 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 means paying special attention to the role of CB in vulcanization as well as to determining the parameters that have a major influence in this process. One of the most widely used and easiest ways to understand how the filler presence can alter the cross-linking reaction is monitoring the curing process in a rheometer. Interesting parameters such as the scorch time, the cross-link degree and the reaction kinetics can be obtained from this test. It is widely known that the presence of CB reduces the scorch time; also its role as a catalyzer accelerating the reaction and obtaining higher reticulation levels has also been accepted in many published papers although a specific mechanism has never been described (figure 5). Although some studies have stated that only the CB loading and not its grade are responsible for the previous modifications, 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⁽⁴⁰⁾ has observed that the cross-link rate constant decreases when the acid concentration on the CB surface increases; some CB structural dependence was also found.

Other analytical tools have also been used to confirm the CB effects on the vulcanization. The group of McGill vulcanized polyisoprene with TMTD 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 cross-link formation rate⁽⁴¹⁾.

On the other hand, Koenig et al. using ¹³C solid state measurements observed that CB might affect the vulcanization mechanism. They suggested that the basic network structure formation could be modified due to cross-link 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⁽⁴²⁾.

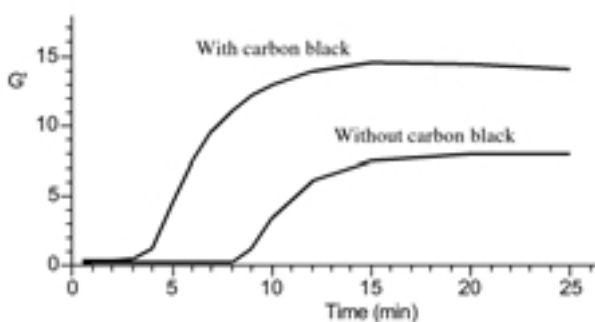


Figure 5. Scorch time reduction and an increase of the crosslinking level reached are two of the most important consequences of CB presence during vulcanization.

In addition, other studies with ¹³C NMR and ¹H transversal relaxation solid state measurements were done on CB filled natural rubber vulcanizates to determine the chemical cross-linking density⁽⁴³⁾. In this case increasing the filler loading seems to decrease the cross-linking density. The authors explained that this effect could be a consequence of the absorption of curing agents 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.

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) is still considered today a useful tool to study polymer reactions and interactions. However it is worth to point out that to obtain reliable results using the MCV approach a suitable low weight molecule must be chosen. Different models for some polymers such as natural rubber, butyl rubber, SBR or EPDM have been described in literature⁽⁴⁴⁻⁴⁸⁾. Using squalene as a MCV for NR the CB presence effect during vulcanization has been studied⁽⁴⁹⁻⁵¹⁾. On one hand, standard CB grades tend to delay the CBS decomposition, this effect could be related to the

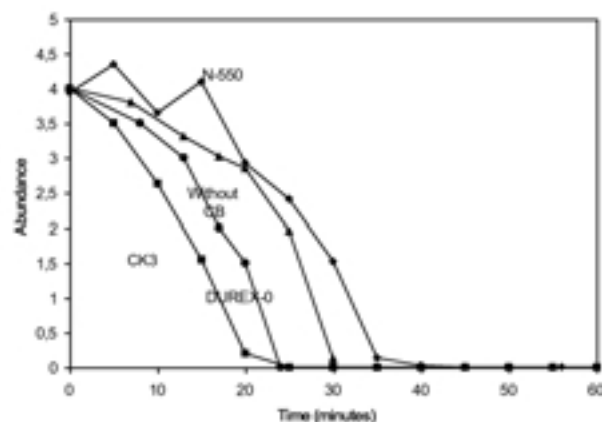


Figure 6. Accelerator decomposition monitoring using MCV approach. Two different trends are observed: regular CB delay the decomposition, while high activity carbon blacks accelerate this process.

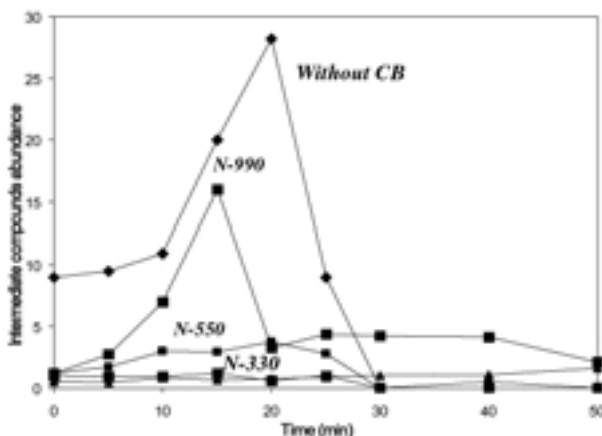


Figure 7. The higher specific surface area, the lower free intermediate vulcanization compounds level is detected by HPLC.

absorption of the vulcanization intermediates on the CB surface, which is also confirmed by a decrease in the detection intensity when the reaction components are analyzed by HPLC. On the other hand CBS decomposes faster when using CB with high surface activity (figure 6). It is interesting to notice that two different processes in competition may be taking place, the specific surface area and the surface activity being the main factors involved. The larger the CB surface for the same activity level, the higher absorption there is at the interphase, and as a result the accelerator decomposition is delayed (figure 7). When the activity plays a more important role, even though the compounds are still absorbed the reaction is accelerated. The fact that the reaction compounds may be present on the CB surface can also cause the vulcanization reaction to show a preference to take place in this location⁽⁷⁾.

Nevertheless, to confirm this hypothesis it would be interesting to try to find out whether, as previously mentioned, such intermediate compounds are really absorbed on carbon black surfaces or not. For this purpose a suitable analytical technique to characterize the filler surface chemical composition accurately at different vulcanization is required.

ToF-SIMS is a surface analysis technique with high sensitivity and it has been used in many research fields. For instance, static SIMS provides information about molecular structure and orientation of polymer chains at the interfaces. Mass spectra of polymers are very characteristic and allow fingerprinting as well as fractional group determination. This technique has been applied to the characterization of different types of CB⁽⁵²⁾. However, not only is it useful to characterize clean CB surfaces, but also to analyze the CB surface during squalene vulcanization reaction⁽⁵³⁾. The results obtained, in agreement with those obtained using HPLC techniques, show that the curing intermediate compounds are strongly absorbed on the carbon black surface (figure 8).

Therefore from these results the following can be concluded: CB may alter the cross-link location due to the intermediates absorption but also could change the reaction kinetics when considering its surface activity and specific surface area. Once again these two parameters seem to play an important role although it has not been completely described.

FURTHER DEVELOPMENTS

All the studies that have been mentioned in this paper although they may not lead to the same conclusions agree that knowledge about CB role in vulcanization and its interaction with polymers is still far from being complete. Surface activity has been demonstrated to have an important influence and the possibility of modifying it, is an interesting way to have a clearer view. Two main factors seem to be involved in the surface activity level. One is the chemical composition of the CB surface that can be responsible for changes in the surface polarity. Techniques such as plasma polymerization can be used to tailor this property by introducing different functional groups that could improve both the reaction and interaction with the polymer matrix. The other variable that may also play a role in the activity phenomenon is the surface morphology which is acquired during the formation process. To modify it, a detailed description of the different energy sites present on the CB surface, but also their process of formation, should be known. Needless to say, the achievement of these results would ensure better properties for rubber materials, which is one of industry's most frequent requirements.

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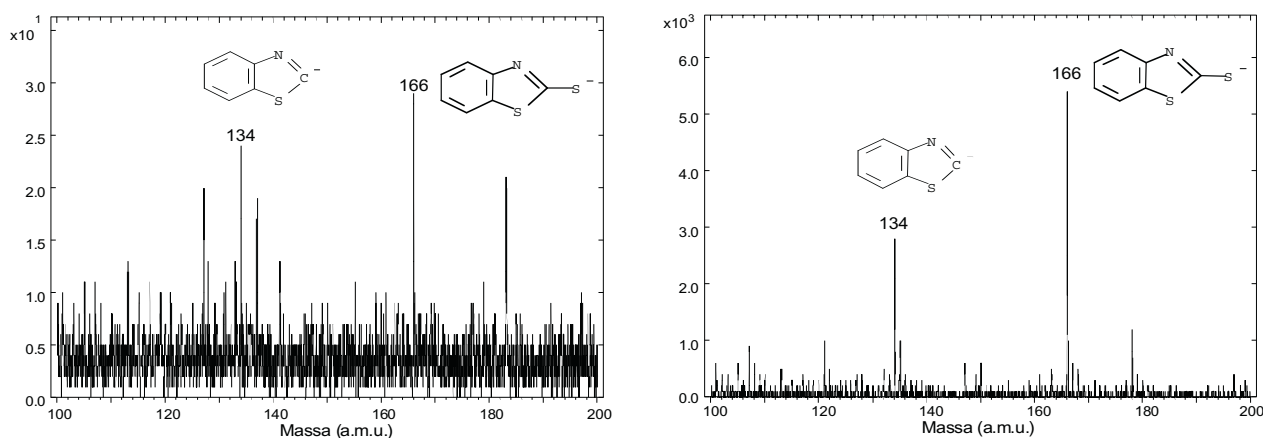


Figure 8. ToF-SIMS analysis allows to confirm the presence of intermediate vulcanization species absorbed on CB surface during squalene vulcanization.

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