

Exploring Tire Crumb as Activator for Sulfur Vulcanization

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ABSTRACT: In this study, a new approach to reduce the environmental effects of end of life and waste rubber and, at the same time, to minimize the ZnO levels in rubber compounds is presented. The use of tire crumb as activator for sulfur vulcanization is investigated. To give an insight into the reaction mechanism, the approach is tested using model compound vulcanization (MCV) with squalene as a model molecule. The results showed that the use of the new recipe does not alter the kinetics of the vulcanization and that the cross-link degree achieved is nearly equivalent to using ZnO. However, in real rubber mixtures [natural rubber (NR), butadiene rubber (BR), and styrene–butadiene rubber (SBR)], there is not a correlation between the promising characteristics seen in MCV and the actual performance of tire crumb. The extent of cross-linking is significantly lower and the mechanical properties are worst in most of the cases. In spite of that, the results found in MCV suggest that further research should be carried out in order to take advantage of the features observed by improving or facilitating the interaction between the chemicals present in the tire crumb and the ingredients added to the rubber matrix. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2809–2820, 2013

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INTRODUCTION

One of the most important environmental related problems in the rubber industry is the management of end of life and waste rubber, especially tires. When tires are taken off vehicles, in some cases, they can be retreaded allowing the tire to start its new life cycle, but mainly the end of life tire is non-reusable in its original form. Due to the chemical cross-linking, it is not possible to simply melt and reshape rubber materials, as can be done with thermoplastics. Furthermore, these materials cannot return to the ecological environment through natural biological degradation, hydrolyzation, or decomposition, like plants or animals, because they degrade very slowly.¹

Landfill was one of the early ways of disposal for discarded rubber products. Landfilling with waste tires is of great concern due to environmental problems caused by leaching of small molecular weight additives that are not eco-friendly and may kill advantageous bacteria of soil and, in addition, the risks from fires and mosquitoes. Nonetheless, disposal of tires in landfills has no future because of the increasingly restrictive legislations.²

The tires can be reused after being processed in different applications such as reinforcing agent in roads^{3,4} and in concrete,^{5–9} particleboard panels,¹⁰ different flooring and play surfaces,¹¹ shoe soles, and so on.

The most common methods to obtain the desulfurization of vulcanized rubber are thermal process, thermomechanical process, mechanochemical process, and chemical process. However, various researches have investigated the possibility of microbial devulcanization processes using different microorganisms.^{12–15} Several reviews available in the literature cover aspects out of the scope of this study such as reclaiming methodologies, grinding and size reduction procedures, and regeneration or devulcanization techniques. From these, the studies of Myhre and MacKillop,¹¹ Adhikari et al.,² Zhan et al.,¹⁶ Noordermeer et al.,¹⁷ and De et al.¹⁸ are recommended.

Another application of main importance is the use of reclaimed or regenerated rubber in blends with virgin rubber. Diverse research studies have investigated the effect of adding ground rubber on the fresh rubber compounds and have been collected by other authors.^{19,20} In addition, collaborative projects have

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been carried out by suppliers of waste tire rubber crumb and research institutes.²¹

A blend of reclaim and virgin rubber would exhibit different properties depending on the grinding procedure and the de-vulcanizing system. In general, these blends cure faster than virgin rubber compound and show less reversion and even antiaging characteristics.² Furthermore, deterioration of the physical properties has been found frequently,^{2,21,22} particularly with increasing amounts of powder. For this reason, it is technically unlikely that the use of scrap tire crumb in new tire compounds could exceed about 10% of the rubber compounds required.¹¹

Nonetheless, it has been reported that the change in scorch time is less in the case of filled compounds.¹⁸ Other studies have shown that the tensile strength and elongation at break of the blends with ultrasonically devulcanized NR were much better than those with the ground rubber.²⁰ It has also been found that the aging conditions of the tire crumbs affect the final properties of the blends.¹⁹

In summary, although there are some contradictory results due to the enormous number of parameters affecting the performance, the use of tire crumb in rubber mixtures is a very important approach to minimize the environmental effect of the rubber industry.

Although several research studies have been carried out with the aim of mixing tire crumb and virgin rubber, no references have been found in the literature regarding the possibility of profiting from the migration of chemicals between the crumb and the matrix to reduce another environmental problem related to the tire industry: the effect of ZnO.

We have already demonstrated^{23,24} that tire crumb is able to activate the vulcanization reaction in the same way that ZnO does, when it is used in model compound vulcanization. In this sense, it has been reported^{25–27} that sulfur and accelerator fragments migrate from the matrix to the particles and vice versa. In this study, this exchange between the crumb and the matrix will be considered as an advantage in order to investigate the possibility of using tire crumb as an activator and, therefore, reduce the zinc levels employed in the rubber compounds by more than a factor of 10.

In order to test this new approach, different techniques will be applied. First model compound vulcanization (MCV) with squalene will be employed to investigate the reaction pathway when tire crumb is used as activator. Squalene has been chosen as model molecule because it consists of six units of isoprene and its molecular weight is relatively high; hence, its structure is more similar to natural rubber polymer chains than other smaller models that consist only of one isoprene unit. However, there is one important difference: in squalene all double bonds are *trans*, and not *cis* as in NR.

Afterwards, different tire crumbs will be mixed with natural rubber (NR), butadiene rubber (BR), and styrene–butadiene rubber (SBR) to study the cure characteristics and the mechanical properties of the vulcanizates. Prior to these tests, different tire crumbs will be characterized.

As it will be seen in the next sections, MCV have suggested that tire crumb could be used as activator and minimize the ZnO levels in rubber compounds. The reaction kinetics and the cross-link degree achieved are nearly equivalent to using ZnO. However, in NR, BR, or SBR compounds there is not a correlation between the promising characteristics observed in MCV and the actual performance of tire crumb. The vulcanization times are shorter but the extent of cross-linking is significantly lower, comparable to the mixtures without activator. In addition, the mechanical properties are worst in most of the cases. Nonetheless, the results found in MCV suggest that further research should be carried out in order to try to take advantage of the features observed by improving or facilitating the interaction between the chemicals present in the tire crumb (ZnO, amines, cross-linked precursors, unreacted curatives accelerators, etc.) and the ingredients added to the rubber matrix.

EXPERIMENTAL

Materials

Squalene (Fluka, 97%), sulfur (Julio Cabrero & Cia, S.L.), *N*-cyclohexyl-2-benzothiazolesulphenamide (CBS, Flexsys), zinc oxide (Red Seal, Zincsa), and stearic acid (Calià&Parés) were used for the model compound studies. Solvents used in the investigation were all HPLC grade: Acetonitrile (J. T. Baker); 2-propanol and *n*-hexane (Panreac).

Natural rubber (Malaysian Rubber, SMR-CV60), butadiene rubber (Buna CB 24, *cis*-1,4 content min. 96%, Lanxess), solution styrene–butadiene rubber (Buna VSL 2525-0, 25% by wt vinyl content, 25% by wt styrene content, Lanxess), zinc oxide (Red Seal, Numinor), sulfur (“Mahlschwefel”, Lanxess), CBS (Vulkacit CZ/C, Lanxess), and stearic acid were used for rubber mixtures.

Tire crumb was provided by two different suppliers, each of them delivering four different tire crumbs. The first supplier contributed with two different rubber reclams (TC1 and TC2) in the form of slabs and two rubber powders (TC3 and TC4), both obtained from truck tire treads. The second supplier delivered four rubber powders (TC5, TC6, TC7, and TC8) from unspecified sources.

Characterization of Tire Crumb

Thermogravimetric analysis (TGA) was performed in a Mettler TG30 (Mettler-Toledo) in order to determine the composition of the tire crumb. Furthermore, from the decomposition temperature (T_d) it is possible to obtain information for the identification of the polymer type. Atomic absorption spectroscopy was employed to quantify the zinc content. It was measured by dissolving the ashes of the different tire crumbs in diluted hydrochloric acid and using an atomic absorption spectrophotometer.

Proton double quantum (DQ; or more generally multiple-quantum, MQ) solid-state NMR spectroscopy has been used to measure the cross-link density of the different tire crumbs. Experiments were carried out at 353 K on a Bruker minispec mq20 spectrometer operating at 0.5 T with 90° pulses of 1.7 μ s length and a dead time of 12 μ s. For more information about this technique, the study of Saalwächter²⁸ and Valentín²⁹ is recommended.

Table I. Model Compound Vulcanization Recipes (phr)

| Ingredients | Mixture A | Mixture B |
|------------------|-----------|-----------|
| Squalene | 100 | 100 |
| CBS | 1.2 | 1.2 |
| Sulfur | 2 | 2 |
| ZnO | 5 | - |
| TC3 ^a | - | 5 |
| Stearic acid | 2 | 2 |

^aTC3: Tire crumb type 3.

Model Compound Vulcanization

Model compound vulcanization with squalene as a model molecule for natural rubber has been chosen to study the role of the tire crumb (TC) along the reaction using CBS as accelerator. The basic vulcanization recipe is given in Table I. The study was performed using the same concentration of ZnO and tire crumb, 5 phr.

The reaction for all formulations was performed in a preheated thermostatic oil bath at 140°C for 60 min. The vulcanization reaction is carried out in different vessels under nitrogen environment in order to avoid the oxidation of the double bonds of squalene. The model mixtures are continuously stirred to assure its homogeneity. During the reaction, vessels are taken from the oil bath at different pre-set times and quickly cold quenched in dry ice to stop the reaction. After cooling, the vessels were covered to avoid any UV influence, and stored in a refrigerator.

All the model compound vulcanization mixtures were characterized by two analytical methods of HPLC coupled to an UV detector to cover both aspects of the process: the fading of the accelerator and the formation of cross-links between the model molecules. The identification of the different compounds [CBS, 2-mercaptopbenzothiazole (MBT), 2,2'-bisbenzothiazole disulphide (MBTS), sulfur, squalene, and the different cross-linked squalenes] was carried out earlier in our research group using different techniques.^{30–35}

Table II. Composition of the NR, BR, and SBR Compounds

| Samples | | | Recipe ^a (phr) | | | | | | | | |
|---------|--------|--------|---------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| NR | BR | SBR | ZnO | TC1 | TC2 | TC3 | TC4 | TC5 | TC6 | TC7 | TC8 |
| MB_NR | MB_BR | MB_SBR | - | - | - | - | - | - | - | - | - |
| NZNO_5 | BZNO_5 | SZNO_5 | 5 | - | - | - | - | - | - | - | - |
| NTC1_5 | BTC1_5 | STC1_5 | - | 5 | - | - | - | - | - | - | - |
| NTC2_5 | BTC2_5 | STC2_5 | - | - | 5 | - | - | - | - | - | - |
| NTC3_5 | BTC3_5 | STC3_5 | - | - | - | 5 | - | - | - | - | - |
| NTC4_5 | BTC4_5 | STC4_5 | - | - | - | - | 5 | - | - | - | - |
| NTC5_5 | BTC5_5 | STC5_5 | - | - | - | - | - | 5 | - | - | - |
| NTC6_5 | BTC6_5 | STC6_5 | - | - | - | - | - | - | 5 | - | - |
| NTC7_5 | BTC7_5 | STC7_5 | - | - | - | - | - | - | - | 5 | - |
| NTC8_5 | BTC8_5 | STC8_5 | - | - | - | - | - | - | - | - | 5 |

^aIngredients in parts per hundred rubber: NR, BR, or SBR 100; stearic acid 2; CBS 1.2; sulfur 2; activator system.

Preparation and Characterization of Rubber Samples

The studied compounds were prepared by two steps. The compositions of the different samples are showed in Table II. First, approximately 500 g masterbatch for each rubber without activator was prepared in a two-roll mill using standard procedures. These masterbatches contain stearic acid (2 phr), CBS (1.2 phr), and sulfur (2 phr). Afterwards, the different activators systems were added to the masterbatches in an internal mixer with Banbury rotors (Thermo Haake Polylab system Reocord/Rheomix 600 Type 557-9300), fill factor 0.75. The software "PolyLab Monitor" has been used for data acquisition. Every formulation was scaled up to 50 g taking into account the density of every ingredient to avoid overpressure problems inside the internal mixer. Temperature was set at 40°C for the cavity and it was controlled during the mixing process avoiding always overcoming 100°C to prevent pre-vulcanization and the speed of the rotors was maintained at 50 Hz.

The sample names, e.g., NTC1_5 encode the type of rubber (N for NR, B for BR, and S for SBR), the activator system (TCx for each different tire crumb, ZNO for ZnO) and the amount of tire crumb or ZnO in phr (5.0 in all cases). Samples MB_NR, MB_SBR, and MB_BR are the masterbatches employed to obtain each sample.

Vulcanization took place at 280 bar in an electric-heated press at the optimum cure time (t_{90}) plus 2 min. t_{90} was deduced from the rheometer curve (Monsanto Rubber Process Analyser, model RPA2000) according to ASTM D2084. The vulcanization temperature was 140°C for natural rubber and 160°C for butadiene rubber and styrene–butadiene rubber.

Stress-strain measurements were performed on dumb-bell shaped specimens (Type 3) according to ISO 37 in a Zwick/Roell Z1010 at a traction rate of 200 mm/min. Five samples were used for the tensile test and an average of the five results was taken as the resultant value.

RESULTS AND DISCUSSION

In order to test the effect of substituting ZnO with tyre crumb, different approaches will be applied. First model compound

vulcanization with squalene will be carried out to investigate the reaction pathway when tire crumb is used as activator. Afterwards, different tire crumbs will be mixed with natural rubber, butadiene rubber, and styrene–butadiene rubber and the cure characteristics and the mechanical properties of the vulcanizates will be analyzed. Prior to these tests, the different tire crumbs used in this study will be characterized.

Characterization of Tire Crumb

A standard tire formulation incorporates a precise blend of different rubbers. However, it also contains a relatively high number of substances like fillers, organic substances as plasticizers, lubricants, antioxidants, vulcanization agents, etc., being each formulation designed for a specific application. This complexity causes the identification of each component and its quantification to be a laborious task. Nonetheless, thermogravimetric analysis (TGA) is a reliable method to obtain an approximate composition of the tire. From the TG and the derivative thermogravimetry (DTG) procedure, the rubber types can be determined. The results can be evaluated only as “approximate” because of the small sample mass used.

Atomic absorption spectroscopy has been employed to measure the zinc content of the samples and double quantum NMR spectroscopy to measure the de-vulcanization degree. For more information regarding these techniques see the Supporting Information. The cross-link density of the tire crumb samples is defined as the partially averaged residual dipolar coupling constant (D_{res}) because the samples contain a mixture of NR and BR and/or SBR (Supporting Information) and for SBR there is not yet an expression relating D_{res} and the molecular weight between constraints (M_c).

Tyre crumbs from two different suppliers have been used in this study. All the samples have around 64 wt % of polymer, 30 wt % of carbon black, and 5 wt % of ashes. The relation between NR and SR is 70/30 in most of the samples. TC4, TC5, and TC7 show a higher NR content and TC8 a slightly higher SR content. The tire crumbs can be classified in two main groups: tire crumbs with 1.5% ZnO and tire crumbs with 3.1% ZnO.

The results found have indicated that there are almost no differences between the different tire crumbs, despite the fact they come from two suppliers which, allegedly, perform different treatments to the samples. The first supplier has provided two rubber reclaims (TC1 and TC2) in the form of slabs and two rubber powders (TC3 and TC4). The second supplier delivered four rubber powders (TC5, TC6, TC7, and TC8).

DQ NMR experiments were performed to measure the (de)vulcanization degree of the tire crumbs in order to find whether the treatments applied cause any difference. Since TC1 and TC2 are (supposedly) rubber reclaims, it is expected that these samples exhibit a low cross-link degree. However, the second supplier maintains that the process applied causes the devulcanization of the sample and, therefore, it is anticipated to detect differences between these samples and TC3 and TC4.

As expected, since TC1 and TC2 are rubber reclaims in the form of slabs, they have the lowest vulcanization degree. TC3 and TC4 have a similar cure extent, higher than TC1 and TC2.

Contrary to what was suggested by the second supplier, their samples have not been devulcanized as much as TC1 or TC2. There are no significant differences compared to the other rubber powders with the exception of TC5, which has the lowest devulcanization degree of the specimens studied.

In summary, the analyses performed in this section have shown that the tire crumbs obtained for this study are similar, both in composition and cross-link density, particularly the rubber powders. In order to perform the model compounds vulcanization studies, TC3 has been chosen. This sample has, in average, the same content of polymer, carbon black, and ashes than the rest of the samples according to the TGA measurements and their risk in representation. In addition, devulcanization degree is at the same level than the average of the rest of rubber powders.

Model Compound Vulcanization

Model compound vulcanization with squalene as a model molecule for natural rubber has been chosen to study the role of tire crumb along the reaction using CBS as accelerator. The basic vulcanization recipe is given in Table I. This study was performed using the same concentration of tire crumb and ZnO, 5 phr.

In Figure 1, it is represented the evolution of the accelerator along the reaction. Comparing the results obtained with standard ZnO and TC3, it can be observed that the reaction rate of this compound is the same in the mixtures with TC3 and standard ZnO. The application of ZnO or TC3 as activators does not influence the breakdown of CBS differently.

To study further the decomposition of the accelerator, the formation of MBT is depicted in Figure 2. As it can be seen, again, the use of ZnO or TC3 does not cause significant differences. When TC3 is used, the formation of MBT commences faster, there are higher amounts of MBT at 30 min. At longer reaction times, these differences disappear and the levels of MBT are harmonized.

It has been reported^{30,36} that the breakdown of the accelerator would not occur until much longer reaction times when ZnO is

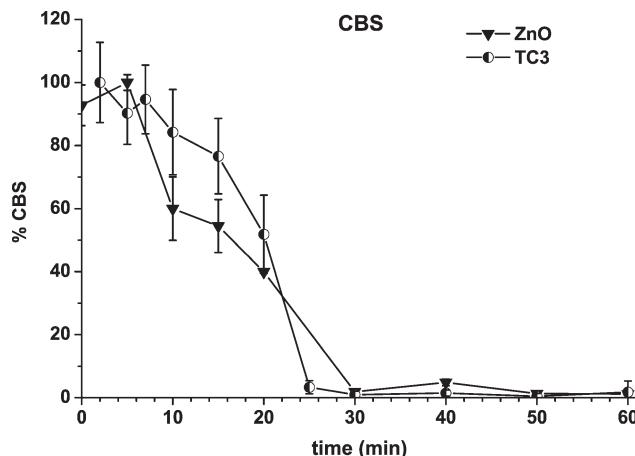


Figure 1. Breakdown of CBS as a function of the reaction time with tire crumb and ZnO as activator.

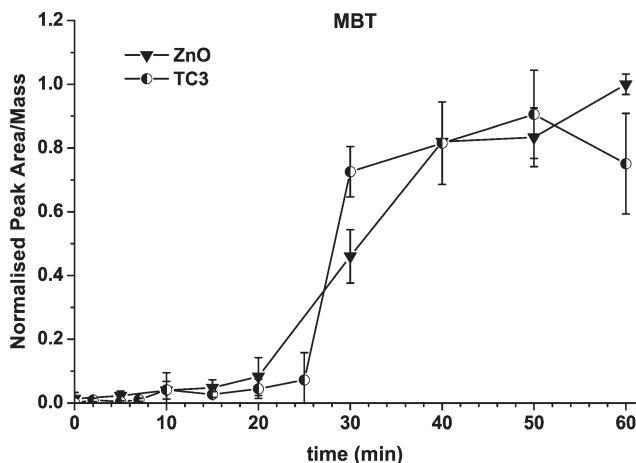


Figure 2. MBT concentration as a function of the reaction time with tire crumb and ZnO as activator.

not present in the recipe. Therefore, the fact that there are almost no differences in the reaction of the accelerator (see Figures 1 and 2) indicates that tire crumb acts as an effective activator for the decomposition of CBS.

Figure 3 shows that the consumption of sulfur starts earlier when TC3 is used as the activator. Sulfur starts to react after 20 min with TC3 and after 30 min with ZnO. Nevertheless, once sulfur has begun to react, the depletion is sharper with ZnO. It takes 20 min for the complete reaction and 30 min with TC3. In both cases, at 50 min, there is no more free sulfur present in the mixture.

The evolution of cross-linked squalene is displayed in Figure 4. When TC3 is used instead of ZnO, it can be appreciated that formation of the cross-linked products commences later and that the cross-link degree attained is reduced. However, the differences in the extent of cure achieved are smaller than working with MgO.³⁷

Regarding the cross-link structure, some changes are observed when TC3 is used. Figure 5 presents the percentage of mono-($Sq-S-Sq$), di-($Sq-S_2-Sq$), tri-($Sq-S_3-Sq$) and tetrasulfidic

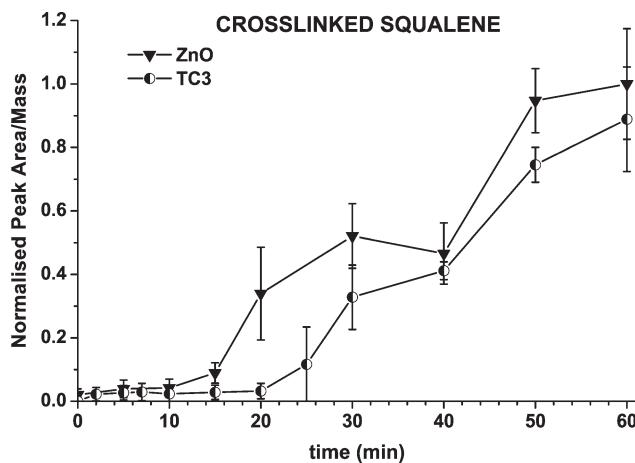


Figure 4. Evolution of total cross-linked squalene during vulcanization with standard ZnO and tire crumb.

($Sq-S_4-Sq$) cross-links in 60 min vulcanizates. The presence of TC3 in the recipe decreases the fraction of mono- and disulfidic cross-links. The reduction of monosulfidic cross-links is more acute, there is a fall from 30% with ZnO to 5% with TC3. In contrast, the proportion of tri- and tetra-sulfidic cross-links is increased, particularly significant in the case of tri-sulfidic cross-links, which rise from 30% to more than 60%.

This could be explained by the fact that the amount of zinc oxide present in the system containing tire crumb is very small. Zinc accelerator complexes are thought to be responsible for the desulfuration of the polysulfidic cross-links.^{38,39} Due to the amount of ZnO is very limited in the recipe with TC, these species are not formed in enough quantities to promote desulfuration and cross-link shortening.

The results found performing model compound vulcanization indicates that tire crumb could be used as activator for sulfur vulcanization and minimize or eliminate completely the ZnO levels in rubber compounds. Through this section it has been demonstrated that tire crumb have some activator character. It has been seen that TC is able to cause the breakdown of the accelerator in the same way that ZnO does. Previous research

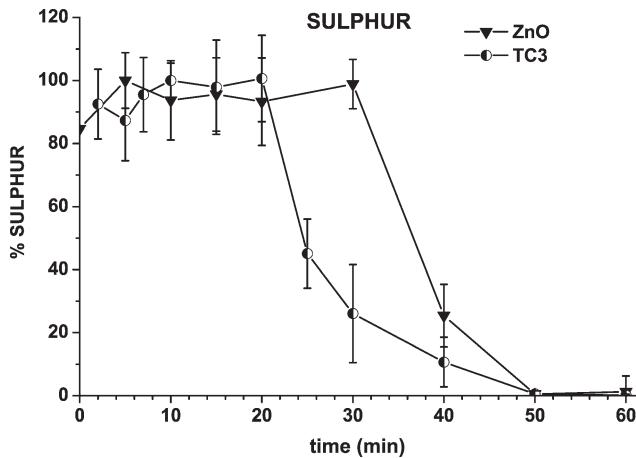


Figure 3. Evolution of sulfur during vulcanization with tire crumb and ZnO.

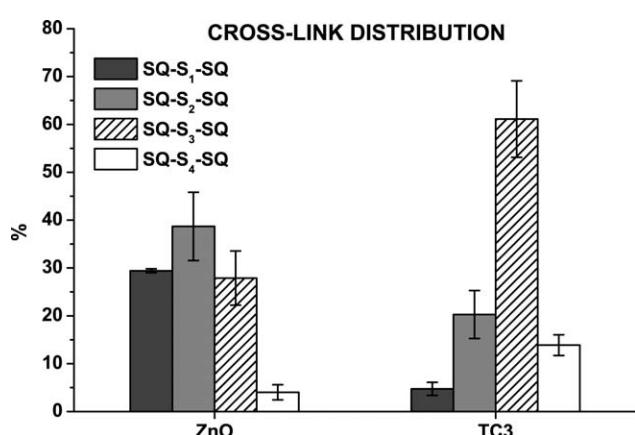


Figure 5. Distribution of cross-links (cross-link structure) in 60 min vulcanizates with ZnO and tire crumb.

studies³⁶ have proved that the breakdown of CBS in MCV with squalene occurs later if no activator is present in the recipe. Accordingly, the fact that CBS reacts similarly with ZnO or TC (Figure 1) indicates that tire crumb possesses some characteristics to perform as an activator. Furthermore, other studies⁴⁰ have shown that MBT is not formed during the vulcanization process in the absence of an activator despite the fact that CBS disappears.

Two main reasons may be the cause of the results found; the presence of ZnO and/or the presence of amines or accelerator residues in the tire crumb. TG experiments have shown that there is around 6% of non-volatile residue or ashes present in the tire crumb. Atomic absorption spectroscopy of the ashes indicates that there is approximately a 3% content of ZnO in TC1, TC2, TC3, and TC4, and around a 1.5% content of ZnO in TC5, TC6, TC7, and TC8. Consequently, the presence of ZnO might be the origin of the activator characteristics shown by tire crumb (Table III).

On the other hand, guanidines and secondary amines in general are sometimes used as secondary accelerators because they increase the vulcanization rate and cross-link density of the primary accelerator. The role of amines is thought to be the formation of coordination compounds with the zinc accelerator complexes.^{41–43} These complexes, being more soluble in rubber, enhance the reactions with sulfur catalyzing the insertion of sulfur to form active sulfurating agents.⁴⁴ The most important guanidine is diphenylguanidine (DPG) which is used mainly as secondary accelerator.⁴⁵ DPG is employed as an activator for sulfenamides and as secondary accelerator in tire tread compounds,⁴⁶ although more commonly in passenger tire treads than in truck tire treads. Furthermore, amines could also be present in the tire crumb as a result of the decomposition of accelerators. Sulfenamides such us CBS or *N-t*-butylbenzothiazole-2-sulfenamide (TBBS) produce amines when they react to form the active sulfurating agents. For that reasons, the presence of amines could also be the cause of the performance shown by TC.

Moreover, sulfenamide accelerators also dissociate to form MBT, which is known for catalyzing the decomposition of CBS.³⁶ It has been reported that the migration of sulfur into the crumb triggers the release of bound accelerator fragments

from the crumb that diffuse into the matrix speeding vulcanization.²⁵

The reactions of the accelerator and sulfur are very similar whether tire crumb or ZnO is added to the recipe. However, the formation of cross-link products is slightly higher and the cross-link distribution of the final vulcanizate is more efficient with ZnO. In spite of this, it should be noted that apart from the variation in the distribution of cross-link, the rest of the parameters studied remains very similar. The cross-link degree attained is even slightly higher than with MgO.³⁷

In order to investigate if tire crumb might replace or substitute ZnO as activator for sulfur vulcanization, different real rubber mixtures containing TC will be prepared to check if the results found with model compound vulcanization are also obtained with actual rubbers.

Rubber Mixtures

Three rubbers have been chosen to study the effect of tire crumb as activator: NR, *cis*-BR, and solution SBR. A masterbatch without activator was prepared for each rubber. Afterwards, 5 phr of tire crumb were added to the mixture obtaining eight samples for each rubber. The compounds were vulcanized according to their optimum vulcanization time and their physical properties were tested. In the following sections, the cure characteristics and the physical properties of the mixtures will be presented and discussed.

Cure Characteristics

Figure 6 shows the rheometric curves for the NR compounds with tire crumb vulcanized at 140°C. The curves of the mixtures with tire crumb are very similar, the scorch and optimal vulcanization times are almost the same. Furthermore, these times are shorter than the compounds without activator or with ZnO. Regarding the extent of cure, tire crumb produces very low ($M_H - M_L$) values, the difference between maximum torque (M_H) and the minimum torque (M_L), on the same level than the masterbatch.

The minimum torque shows a slight increase with TC compare to ZnO-containing samples. This is an indication that the samples are more complicated to process. The increase might be due the rubber powders tend to agglomerate in the matrix

Table III. Composition and Cross-link Density of the Different Tire Crumbs

| Sample | Polymer content (%) | Carbon black content (%) | Ashes content (%) | NR (%) | SR (%) | Zn content (%) | Cross-link density, D_{res} (Hz) |
|--------|---------------------|--------------------------|-------------------|--------|--------|----------------|------------------------------------|
| TC1 | 64.1 | 28.8 | 6.3 | 68.2 | 31.8 | 1.5 | 153 ± 4 |
| TC2 | 67.0 | 26.6 | 6.2 | 70.7 | 29.3 | 1.5 | 152 ± 4 |
| TC3 | 62.5 | 31.1 | 5.7 | 70.6 | 29.4 | 1.5 | 245 ± 6 |
| TC4 | 59.6 | 28.3 | 10.0 | 76.0 | 24.0 | 1.5 | 261 ± 8 |
| TC5 | 64.3 | 29.6 | 6.5 | 79.7 | 20.3 | 3.1 | 326 ± 12 |
| TC6 | 64.7 | 31.1 | 4.4 | 69.1 | 30.9 | 3.1 | 237 ± 7 |
| TC7 | 64.2 | 31.0 | 4.9 | 77.1 | 22.9 | 3.1 | 273 ± 11 |
| TC8 | 64.8 | 30.2 | 5.3 | 63.9 | 36.1 | 3.1 | 240 ± 9 |

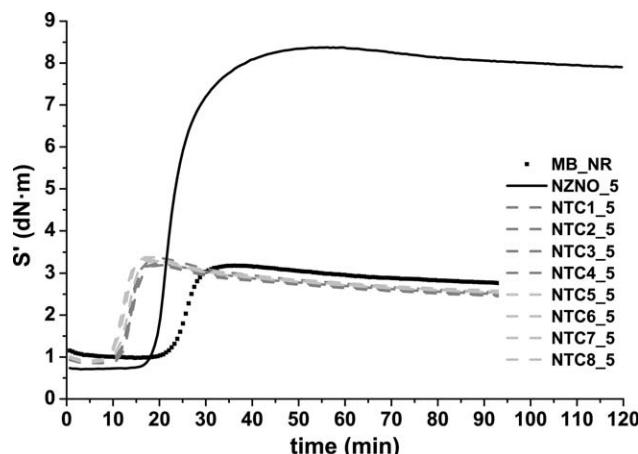


Figure 6. Cure characteristics of NR compounds with tire crumb and ZnO at 140°C.

although TC1 and TC2 are not rubber powder but rubber reclaims in the form of slabs.

It is clear from Figure 6 that the effect of tire crumb as activator is not as it has been detected in model compound vulcanization. Working with squalene it has been found that the reactions of the accelerator and sulfur are faster. This could explain why the scorch times of the mixtures with TC are shorter. Some authors^{25–2747} have suggested that the presence of cross-linked precursors and unreacted curatives accelerators in the rubber powders is the cause of the shortening of the scorch times and optimum vulcanization times. It has been reported that using peroxide-cured particles no reduction in scorch time is detected.¹⁸

On the other hand, in MCV, the total amount of cross-linked squalene was very similar comparing TC and ZnO, but the extent of cure in natural rubber is very different. The samples with TC give $M_H - M_L$ values equivalent to working without activator. These results suggest that the ZnO present in the tire crumb is not able to interact with the accelerator in the same manner as it occurs in MCV.

As it has been explained previously, the presence of amines in the tire crumbs enhances the cross-link degree. However, it is

important to notice that the role of the amines have been associated to the coordination with zinc complexes.^{38,39} Therefore, if zinc oxide is not able to assist in the formation of active sulfurating agents or cross-link precursors, the amines will not cause an increase in the extent of cure.

Table IV summarizes the vulcanization parameters of the natural rubber mixtures. Concerning the reversion resistance, from the data collected in Table IV, it can be perceived that tire crumb deteriorates the reversion behavior in NR compounds. The reversion times and the reversion tax are similar for the different tire crumbs tested. The reversion time is shorter when TC is used compared to the masterbatch without activator or with ZnO. In addition, the reversion tax is increased.

In relation to the different types of tire crumb used as activator, it is worth stating that there are no significant changes in the results. The main important variation between the samples is the devulcanization degree. It has been reported⁴⁷ that there is a weak interaction and bonding between the rubber powder particles and the natural rubber matrix due to little formation of interfacial sulfur cross-links. TC1 and TC2 have a lower cross-link density and this was thought to cause an improvement of the interaction between the rubber matrix and the tire crumb. At it has been stated in the “Introduction” section, it has been reported that blends with ultrasonically devulcanized natural rubber produce better properties than those with the ground rubber.²⁰ Conversely, no improvement has been observed.

Figure 7 shows the rheometric curves for the BR compounds with tire crumb vulcanized at 160°C. As it has been found in the case of NR, there are almost no differences between the curves of the mixtures with TC. The scorch and t_{90} times are virtually the same and slightly shorter than the compounds without activator or with ZnO. In the case of BR, the extent of cure is even reduced compared to the masterbatch.

The vulcanization parameters of the BR mixtures are compiled in Table V. The data displayed reveals that the cure rate index is enhanced if tire crumb is added to the recipe. Considering the reversion exhibited by the BR compounds tested in this work it is interesting to notice the different behavior observed in the reversion times and the reversion tax. The samples with TC give

Table IV. Vulcanization Parameters of NR Compounds Vulcanized with Different Tire Crumbs

| Sample | t_{02} (min) | t_{s2} (min) | t_{90} (min) | CRI (%) | RT (min) | Reversion tax (%) | $M_H - M_L$ (dN·m) |
|--------|----------------|----------------|----------------|---------|----------|-------------------|--------------------|
| MB_NR | 19.6 | 29.3 | 29.2 | - | 12.2 | 12.4 | 2.2 |
| NZNO_5 | 17.1 | 21.0 | 33.3 | 11.7 | 45.2 | 3.8 | 7.7 |
| NTC1_5 | 9.8 | 15.1 | 15.8 | - | 5.5 | 19.6 | 2.4 |
| NTC2_5 | 9.2 | 15.4 | 15.8 | - | 5.5 | 19.5 | 2.3 |
| NTC3_5 | 9.2 | 16.0 | 16.4 | - | 6.7 | 18.3 | 2.3 |
| NTC4_5 | 10.4 | 15.3 | 16.1 | - | 5.2 | 21.0 | 2.5 |
| NTC5_5 | 8.0 | 14.0 | 14.7 | - | 4.9 | 21.0 | 2.5 |
| NTC6_5 | 8.6 | 15.0 | 15.6 | - | 4.6 | 20.8 | 2.4 |
| NTC7_5 | 8.6 | 13.5 | 14.2 | - | 4.3 | 21.3 | 2.5 |
| NTC8_5 | 7.4 | 13.5 | 14.2 | - | 5.5 | 20.7 | 2.4 |

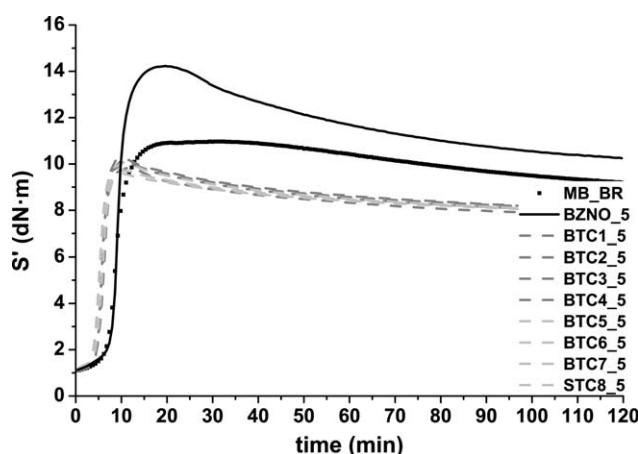


Figure 7. Cure characteristics of BR compounds with tire crumb and ZnO at 160°C.

shorter reversion times but also lower reversion taxes compared to the compound with ZnO. This indicates that when the samples are over cured, those containing tire crumb present a decay of torque very rapidly. Nevertheless, this decrease is moderated if samples are exposed to over curing for longer time. In contrast, the mixture with ZnO has a longer reversion time and a higher reversion tax.

Figure 8 shows the vulcanization curves of SBR with TC vulcanized at 160°C. As it was observed with the other kind of rubber tested in this study, tire crumb causes a decrease in the vulcanization times. Despite the fact that the sample exhibit marching modulus, both scorch and t_{90} times are shorter. Regarding the extent of cross-linking, SBR mixtures containing TC have smaller $M_H - M_L$ and, as in the case of BR, lower than the masterbatch.

Table VI summarizes the vulcanization parameters of the SBR mixtures. Concerning the reversion resistance, since the masterbatch and the compounds with TC show marching modulus, the reversion times, and the reversion tax are not shown. The fact that the rheometric curves for the SBR samples with TC exhibit marching modulus also causes that the CRI is reduced in comparison to the samples with ZnO.

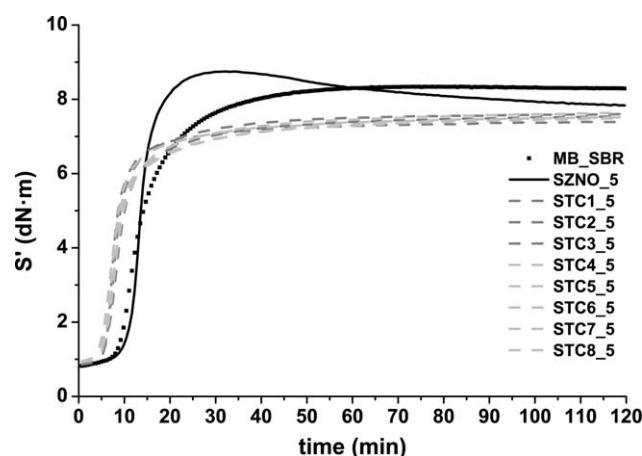


Figure 8. Cure characteristics of SBR compounds with tire crumb and ZnO at 160°C.

Physical Properties

Stress-strain measurements were performed on the mixtures of natural rubber vulcanized at 140°C.

Figure 9 displays the tensile strength (TS), the elongation at break (E_b), and the tensile moduli [modulus at 50% elongation (M_{50}), at 100% elongation (M_{100}), at 200% elongation (M_{200}), at 300% elongation (M_{300}), and at 500% elongation (M_{500})] of the NR compounds. The tensile strength and elongation at break values of the samples containing TC are lower than the masterbatch indicating that the mechanical properties are deteriorated by the presence of tire crumb. On the other hand, the tensile moduli are slightly higher if TC is present in the mixture, especially in the modulus at 500% elongation (M_{500}).

The different types of tire crumb do not cause significant differences in the values of TS and E_b indicating that neither the composition nor the devulcanization degree exert an influence. However, minor differences are found in the tensile moduli. NTC1_5 and NTC2_5 have lower M_{500} than the other samples. As it has been explained previously, TC1 and TC2 have a higher devulcanization degree than the rest of the TC. Therefore, from Figure 9, it can be deduced that when reclaim crumbs are used the tensile moduli at high elongations are slightly lowered.

Table V. Vulcanization Parameters of BR Compounds Vulcanized with Different Tire Crumbs

| Sample | t_{02} (min) | t_{s2} (min) | t_{90} (min) | CRI (%) | RT (min) | Reversion tax (%) | $M_H - M_L$ (dN·m) |
|--------|----------------|----------------|----------------|---------|----------|-------------------|--------------------|
| MB_BR | 3.1 | 7.6 | 12.6 | 20.1 | 28.1 | 5.3 | 9.9 |
| BZNO_5 | 3.1 | 8.1 | 12.1 | 27.3 | 8.8 | 15.8 | 13.1 |
| BTC1_5 | 2.5 | 5.2 | 7.5 | 43.5 | 6.7 | 13.5 | 8.7 |
| BTC2_5 | 2.5 | 5.3 | 7.2 | 52.6 | 6.1 | 14.0 | 9.1 |
| BTC3_5 | 2.5 | 5.4 | 7.7 | 44.1 | 8.5 | 13.0 | 8.9 |
| BTC4_5 | 3.1 | 5.3 | 7.3 | 49.8 | 6.1 | 14.1 | 8.9 |
| BTC5_5 | 2.5 | 4.6 | 6.9 | 43.1 | 6.7 | 13.7 | 8.8 |
| BTC6_5 | 2.5 | 5.1 | 7.5 | 42.2 | 8.5 | 12.2 | 8.5 |
| BTC7_5 | 2.5 | 4.6 | 6.9 | 43.1 | 11.0 | 10.7 | 8.4 |
| BTC8_5 | 2.5 | 4.5 | 6.7 | 45.9 | 8.9 | 11.8 | 8.6 |

Table VI. Vulcanization Parameters of SBR Compounds Vulcanized with Different Tire Crumbs

| Sample | t_{02} (min) | t_{s2} (min) | t_{90} (min) | CRI (%) | RT (min) | Reversion tax (%) | $M_H - M_L$ (dN·m) |
|--------|----------------|----------------|----------------|---------|----------|-------------------|--------------------|
| MB_SBR | 5.6 | 11.0 | 29.2 | 5.5 | - | 0.5 | 7.5 |
| SZNO_5 | 6.8 | 12.3 | 18.9 | 16.4 | 13.4 | 25.0 | 7.9 |
| STC1_5 | 3.7 | 7.1 | 16.9 | 10.2 | - | - | 6.5 |
| STC2_5 | 3.7 | 7.4 | 21.1 | 7.3 | - | - | 6.7 |
| STC3_5 | 3.7 | 7.8 | 25.1 | 5.8 | - | - | 6.6 |
| STC4_5 | 3.7 | 7.3 | 25.7 | 5.4 | - | - | 6.6 |
| STC5_5 | 3.1 | 7.0 | 21.5 | 6.9 | - | - | 6.7 |
| STC6_5 | 3.7 | 7.5 | 26.0 | 5.4 | - | - | 6.6 |
| STC7_5 | 3.1 | 6.6 | 27.7 | 4.7 | - | - | 6.6 |
| STC8_5 | 3.1 | 6.7 | 26.1 | 5.2 | - | - | 6.6 |

In Figure 9, it can also be seen that the sample containing ZnO (NZNO_5) in the mixture exhibit much higher moduli and tensile strength. Since the cross-linking degree values are greater for the sample containing ZnO as activator this behavior is not unexpected. The differences in the tensile moduli are especially greater at high elongations. Regarding the E_b , it can be observed that when ZnO is used as activator the elongation at break reached is significantly lower.

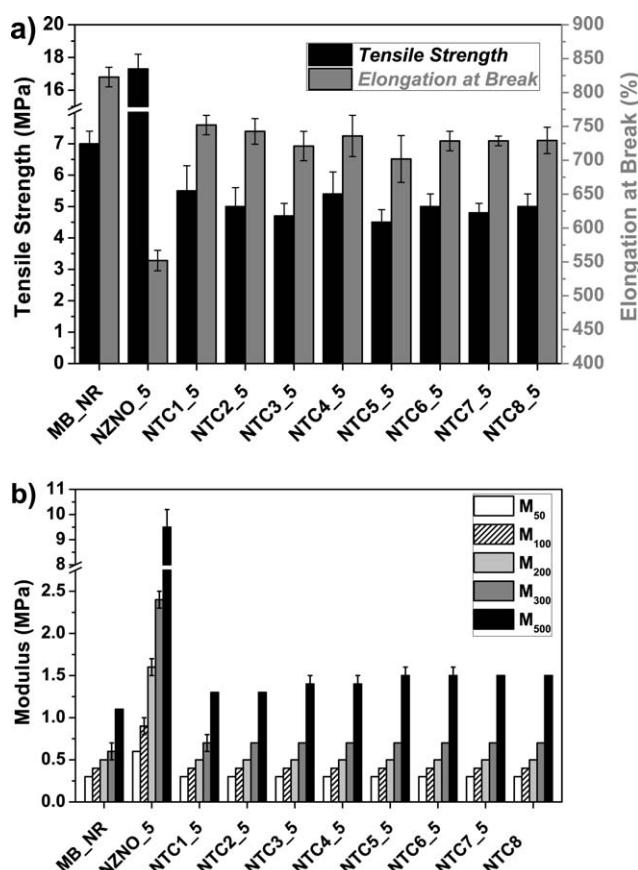


Figure 9. Effect of tire crumb on (a) tensile strength and elongation at break and (b) tensile moduli (M_{50} , M_{100} , M_{200} , M_{300} , and M_{500}) in NR compounds vulcanized at 140°C.

The tensile strength, the elongation at break and the tensile moduli [modulus at 50% elongation (M_{50}) and at 100% elongation (M_{100})] of the BR compounds vulcanized at 160°C are shown in Figure 10. Tensile strength and elongation at break are higher for the mixtures comprising TC, contrary to what has been found in NR samples. In contrast, the tensile moduli are basically equivalent to the masterbatch. When ZnO is present in the mixture, the tensile moduli are higher than the rest of the

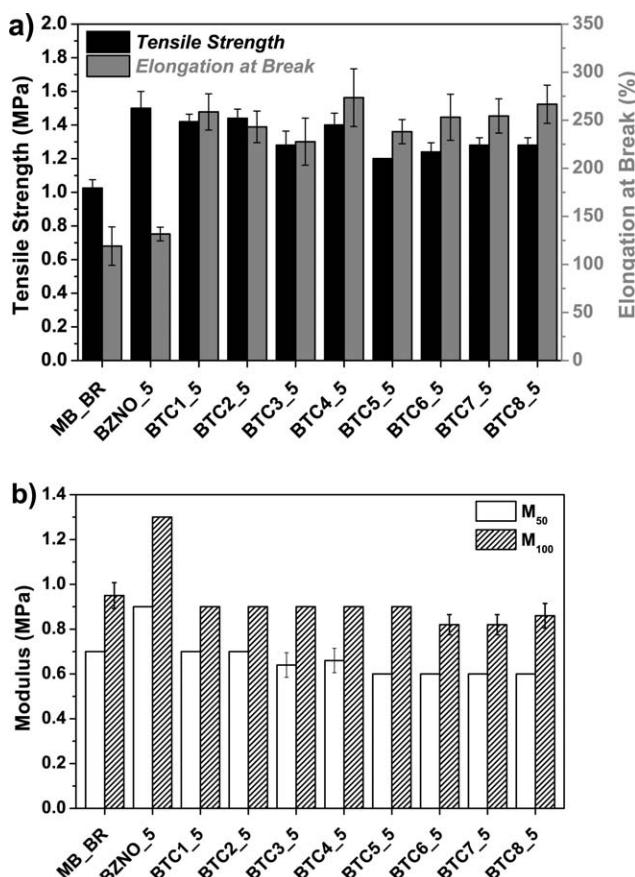


Figure 10. Effect of tire crumb on (a) tensile strength and elongation at break and (b) tensile moduli (M_{50} and M_{100}) in BR compounds vulcanized at 160°C.

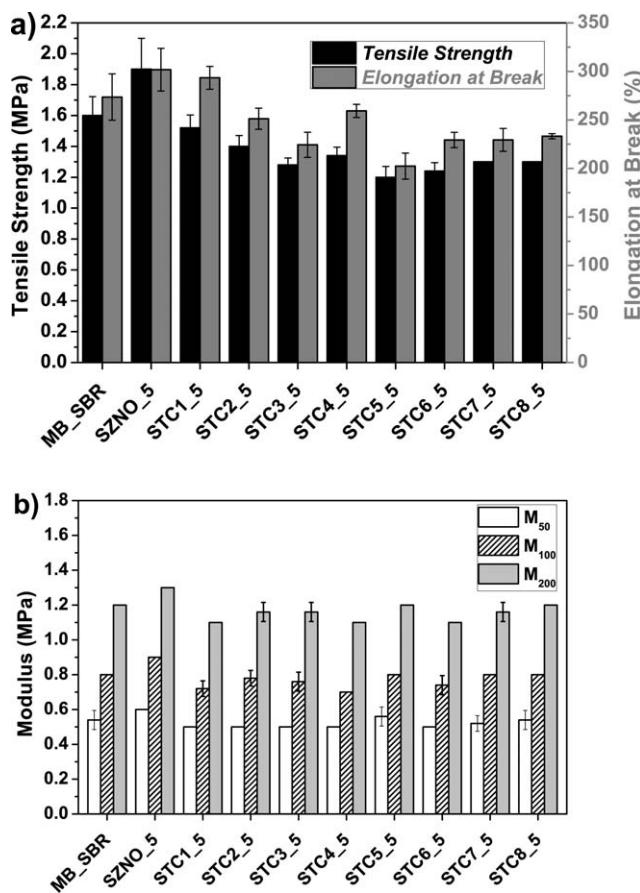


Figure 11. Effect of tire crumb on (a) tensile strength and elongation at break and (b) tensile moduli (M_{50} , M_{100} , and M_{200}) in SBR compounds vulcanized at 160°C.

compounds. The TS is higher if ZnO is added to the compound, however, the differences with respect the TC samples are not as significant as it has been found in NR. The E_b attained is similar to the masterbatch.

In SBR mixtures vulcanized at 160°C, tensile strength and elongation at break are worsened in comparison to the compound without activator as it can be perceived in Figure 11. Nevertheless, no remarkable differences are appreciated in the tensile moduli. In comparison with sample with 5 phr of ZnO (SZNO_5), the differences in the tensile moduli [modulus at 50% elongation (M_{50}), at 100% elongation (M_{100}), and at 200% elongation (M_{200})] and in the elongation at break reached are not very pronounced although the tensile strength is higher.

The results found in this section indicate that the use tire crumb as activator in real rubber mixtures is not as effective as it has been observed in model compound vulcanization. The scorch times are shorter in all the rubber samples tested and the optimum vulcanization times are shorter for natural and *cis*-butadiene mixtures. However, it is worth noting that if longer scorch safety is an important parameter to take into consideration, filled compounds would show a minor change in scorch times.¹⁹

The most remarkable drawback found in the vulcanization curves is the extent of cure achieved, which is significantly

lower. This outcome is more considerable working with NR. In spite of this, in BR and SBR the difference between the masterbatches and the recipes with ZnO is not as important as in NR.

These divergences between MCV and real rubber samples might arise because the ZnO present in the tire crumb is not able to interact with the accelerator in the same manner as it occurs in MCV. As it has been stated before, there is a weak interaction and bonding between the rubber powder particles and the matrix. In MCV, since there are no problems such as agglomeration or dispersion in the matrix, the interaction between the curatives in the tire crumbs and the accelerator is higher and, therefore, the extent of cure achieved is not as worsened as it occurs with the rubbers tested. In addition, swelling of squalene into the rubber particles could be also responsible for the better interaction observed.

The effect of cure-system changes in BR and SBR compounds are not as pronounced as they are in the case of natural rubber.⁴⁸ It has been proposed that in BR and SBR the mechanism seems to be closer to the pathway of unaccelerated sulfur vulcanization, with less involvement of zinc-accelerator species and the appearance of radical reactions.⁴⁹ For that reason the differences between MCV and BR and SBR mixtures caused by the substitution of ZnO by tire crumb cause that are not as significant as in NR.

Regarding the mechanical properties, it has been seen that the effect of adding tire crumb to the recipe is detrimental in most of the cases. Only the tensile strength of the BR compounds has been slightly improved. Comparing with the results found with ZnO as activator, it is clear that the physical properties of the compounds containing TC are not comparable to standard formulations with ZnO, especially for NR. Different researchers²² have shown that adding tire crumb to the recipes produces a decrease in the mechanical properties of NR compounds containing ZnO. The properties of the mixtures with tire crumb were not expected to be on the same levels as with ZnO. However, taking into account the results obtained in the MCV studies, it was not anticipated to find no differences with the compounds without activator.

CONCLUSIONS

Model compound vulcanization studies have suggested that tire crumb could be used as activator for sulfur vulcanization and minimize the ZnO levels in rubber compounds. The breakdown of the accelerator and the consumption of sulfur occur in the same way that when ZnO is used. The cross-link degree achieved, calculated as the total amount of cross-linked squalene, is slightly higher with ZnO and the cross-link distribution in the final product is more efficient. Nevertheless, the differences, especially in the extent of cure, are not significant enough to prevent the use of tire crumb as activator.

In NR, BR, or SBR compounds there is not a correlation between the promising characteristics observed in MCV and the actual performance of tire crumb. The scorch and optimum vulcanization times are shorter but the extent of cross-linking is significantly lower, comparable to the mixtures without activator. In the case of natural rubber, the effect on the degree of

cure is more prominent, showing a noticeable reduction when tire crumb is used as activator. In addition, the mechanical properties are worst in most of the cases.

It is difficult to avoid the use of ZnO as activator for NR vulcanization because it plays an essential role in the three key steps of the curing process. It is an important substance for the formation of the active sulfurating agents and the cross-links and, in addition, in the reactions that lead to cross-link shortening and cross-link degradation.

In rubber mixtures containing only a synthetic rubber, such as styrene–butadiene rubber or butadiene rubber, the effects of cure-system changes may not be as pronounced as they are in the case of natural rubber.⁴⁸ It has been proposed that in BR and SBR the mechanism seems to be closer to the pathway of unaccelerated sulfur vulcanization, with less involvement of zinc-accelerator species and the appearance of radical reactions.⁴⁹ For that reason, the substitution of ZnO by tire crumb is less detrimental in the case of synthetic rubber.

However, the promising results found in MCV suggest that further research should be carried out in order to try to take advantage of the features observed by improving or facilitating the interaction between the chemicals present in the tire crumb (ZnO, amines, cross-linked precursors, unreacted curatives accelerators, etc.) and the ingredients added to the rubber matrix.

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