

Control of Vulcanizing/Devulcanizing Behavior of Diphenyl Disulfide with Microwaves as the Heating Source

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ABSTRACT: Diphenyl disulfide is a common agent used in the devulcanization of sulfur-vulcanized goods. Its activity has been tested both in real rubber samples and in model molecules but, to the best of our knowledge, always under normal heating conditions. Moreover, there is a lack of information about how the vulcanizing potential of the molecule can affect the devulcanization yield. In this study, the diphenyl disulfide behavior has been studied in model compound vulcanization, with squalene used as a model

molecule of natural rubber. Microwaves have been used as a heating source, and the vulcanization/devulcanization behavior of the molecules has been characterized. The results have shown that it is possible to tailor the diphenyl disulfide activity by controlling the reaction temperature and also through microwave power control. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1969–1975, 2008

Key words: recycling; rubber; vulcanization

INTRODUCTION

The process of rubber devulcanization has a long history, but during the past 10 years, renewed interest in the subject has arisen, mainly because of the increased public and regulatory concerns for properly managing rubber wastes. This process should be understood as a potential method for recycling rubber wastes, that is, making it possible to obtain rubber materials that can be vulcanized again and used for other applications.¹ Furthermore, it would be very important to gain insight into the reaction mechanisms occurring during the devulcanization process to be able to optimize and better understand it.

When one tries to establish the status of the research and development of devulcanization technologies, such methodologies can be grouped into categories such as chemical, ultrasonic, microwave, and biological. So far, most of the methodologies described in the literature to devulcanize rubber have been applied only on laboratory to pilot plant scales. In addition, nearly all the approaches studied have shown some difficulties; among others, the

processes are too slow, are very inefficient, or become too expensive to be implemented on an industrial scale.^{2,3}

This article is focused on the efforts made to characterize the devulcanization mechanism when diphenyl sulfide (DPDS) is used as a devulcanizing chemical and how the heating system is able to control its reactivity. This devulcanizing agent is commonly used in the devulcanization of sulfur-vulcanized goods.^{4–9}

The results presented in this work were obtained with the model compound (MC) approach, which consists of using a low-molecular-weight compound (squalene) to simulate the behavior of the real polymer. This working methodology is widely used in this field, and several compounds have already been used as models for different polymers for sulfur vulcanization.^{10,11} The main advantage of such an approach has to do with the complexity of sulfur-accelerated vulcanization. There are two main difficulties with which scientists have to deal: the nature of rubber samples and the large number of reactions that take place simultaneously. To simplify the study, this so-called modeling approach has been traditionally used. Because most of the time we are dealing with liquid samples, better sample handling is allowed, and a wider range of analytical techniques can be applied. Our group has wide experience working with such an approach for studying the vulcanization mechanism of natural rubber.^{12,13}

Different heating methods have been tested and shown very promising results, pointing out the ability

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to use microwaves to control the behavior of the so-called devulcanizing agent. Thus, through the combined use of a devulcanizing chemical and microwaves, it seems to be possible to produce novel elastomeric formulations.

EXPERIMENTAL

Materials

Squalene (Fluka, Buchs, Switzerland; 97%) was used for this study without further purification. Sulfur, *N*-cyclohexylamine-2-benzothiazole (CBS), zinc oxide (ZnO), and stearic acid were provided by Jevsa (Castellbisbal, Barcelona, Spain) and used for the vulcanization of MC. DPDS (Fluka, Buchs, Switzerland; 97%) was used without further purification. The solvents used in the investigation were acetonitrile (J. T. Baker, Phillipsburg, NJ), tetrahydrofuran (THF; Merck, Darmstadt, Germany), and 2-propanol and *n*-hexane (Panreac, Barcelona, Spain). All were high-performance liquid chromatography (HPLC) grade.

MC mixtures

The experiments were carried out with a vulcanizing system containing a single accelerator: CBS. The vulcanization recipe is given in Table I. CBS was also substituted by the same amount of diphenyl disulfide (DPDS) in the recipe given in Table I to test DPDS as a vulcanization/devulcanization agent, and the results were compared with those of CBS. For the conventional heating experiments, the vulcanization reaction was carried out in different vessels. A thermostatic oil bath was used to control the reaction temperature. The model mixtures were continuously stirred to ensure their homogeneity, and a nitrogen atmosphere was used to avoid oxidation of the double bonds of squalene. During the reaction, every vessel was taken out from the oil bath at previously determined reaction times. They were quickly cold-quenched to stop the reaction.

A commercially available microwave oven (Discover model focused microwave synthesis system, CEM Corp., Matthews, NC) was used for the microwave heating experiments. As with conventional heating, vulcanization was carried out in a closed vessel in a nitrogen atmosphere, and the model mix-

ture was continuously stirred to ensure its homogeneity. The equipment could work in two different modes: power-time and standard. In the former, the power and time were fixed, whereas the temperature changed during the reaction. In the latter, the temperature remained constant during the reaction time, and the power varied with the time to maintain this temperature. In this case, a standard-mode method was developed, with the temperature fixed at 140°C, and the maximum pressure was set at 15 bar. The maximum power was set at 300 W, and it was varied during the reaction to maintain the temperature at 140°C. This microwave oven included an infrared temperature sensor that permitted the control of this variable. During the reaction, these parameters were monitored to control the reaction and its repeatability. All the mixtures were quickly cold-quenched to stop the reaction at the predetermined time.

Both formulations (containing CBS and DPDS) were heated for 60 min at 140°C with both heating methods to study the vulcanization behavior. After that, the resulting mixtures were heated for another 60 min at 200°C for reversion studies.

Analytical strategy

All the mixtures were characterized by two analytical methods, HPLC and gel permeation chromatography (GPC), to cover both aspects of the process, the disappearance of the accelerator and the formation of crosslinks between the model molecules.

Characterization of the accelerator reaction

A Merck-Hitachi T-6300 column thermostat chromatograph (Darmstadt, Germany) coupled to a Merck-Hitachi L-4000 UV detector was used to analyze the concentration of the accelerator and the active sulfurating agents.¹⁴ The UV detector was set at 254 nm, and the mobile phase was acetonitrile/water (90:10). Samples were prepared as follows: 0.1 g of the cold-quenched vulcanizate was dissolved in 5 mL of acetonitrile for 5 min in an ultrasonic bath at room temperature. Before injection, samples were filtered with a 0.45- μ m nylon filter to remove insoluble particles that would damage the column. The mobile phase flow was 1 mL/min, and the injection volume was 20 μ L. A Kromasil 100 C18 column (Sant Cugat, Spain) (5 μ m, 15 \times 0.4 cm²) was used. As shown in Figure 1, the presence of 2-mercaptobenzothiazole (MBT), CBS, dibenzothiazole disulfide (MBTS), and sulfur could be detected. The peaks appearing between 5 and 8 min corresponded to active sulfurating agents. The higher the elution time was, the higher the sulfur content was. The same method was used to follow DPDS and its active sulfurating agents. The identification of the chromatographic peaks is shown in Figure 2.

TABLE I
MC Vulcanization Recipe

Ingredient	Concentration (phr)
Squalene	100
CBS (or DPDS)	2
Sulfur	2
ZnO	5
Stearic acid	2

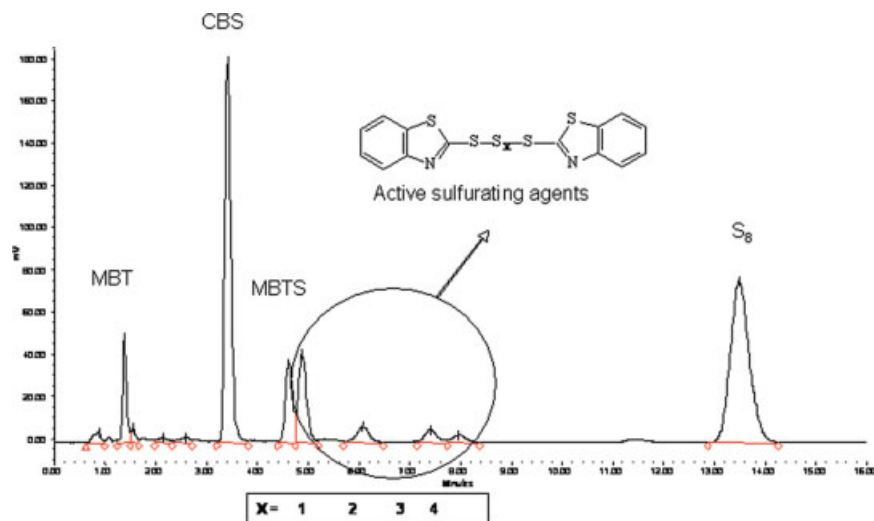


Figure 1 HPLC–UV analysis of the vulcanization of squalene with CBS with a 2-min hold time, a wavelength of 254 nm, a 20- μ L injection volume, and acetonitrile/water (90 : 10) as an eluent. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Characterization of the squalene behavior

Another HPLC–UV method used was optimized to study the polysulfidic crosslink formation and the evolution of squalene.¹⁵ The UV detector was set at 230 nm, and the mobile phase was acetonitrile/2-propanol/*n*-hexane (72 : 17 : 11). Samples were prepared as follows: 0.1 g of the cold-quenched vulcanizate was dissolved in 10 mL of eluent for 5 min in an ultrasonic bath at room temperature. Before injection, samples were filtered with a 0.45- μ m nylon filter to remove insoluble particles that would damage the column. A Kromasil 100 C18 column 5 μ m, 25

\times 0.4 cm was used. A chromatogram of a mixture heated 20 min with microwaves with the peaks identified by mass spectrometry is presented in Figure 3 for the CBS system. The peaks appearing between 4 and 6.3 min were identified as crosslinked squalene.

Given the fact that squalene has quite a high molecular weight (410 g/mol), GPC was thought to be a suitable technique to follow its crosslinking. An analytical method was optimized, in our research group, to follow the vulcanization process.¹² GPC experiments were carried out in a Merck-Hitachi T-6300 column thermostat chromatograph coupled

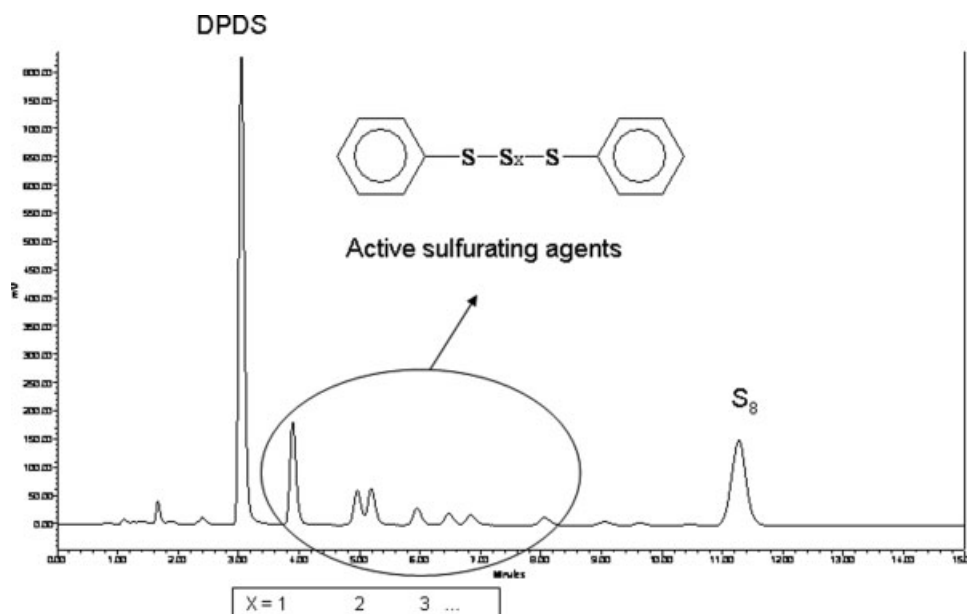


Figure 2 HPLC–UV analysis of the vulcanization of squalene with DPDS with a 2-min hold time, a wavelength of 254 nm, a 20- μ L injection volume, and acetonitrile/water (90:10) as an eluent.

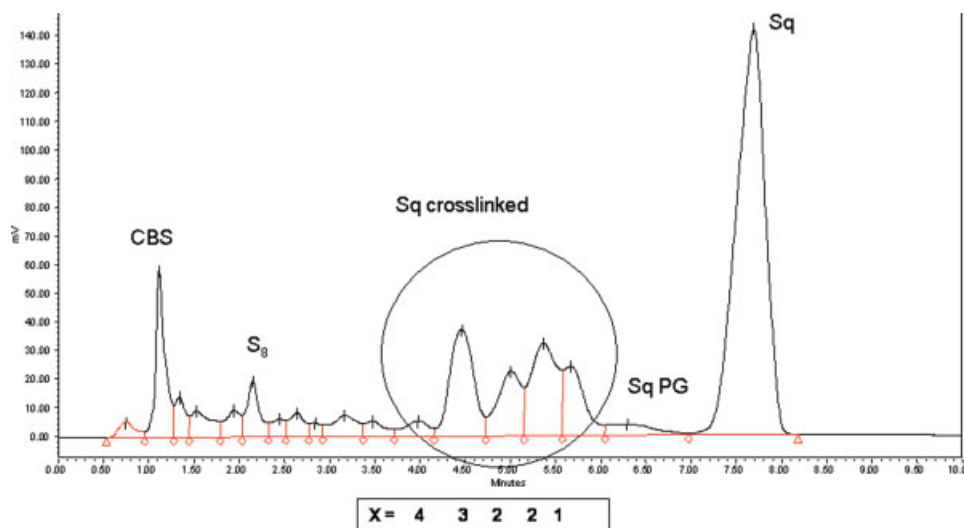


Figure 3 HPLC-UV analysis of the vulcanization of squalene (Sq) with CBS with a 20-min hold time, a wavelength of 230 nm, a 20- μ L injection volume, and acetonitrile/2-propanol/*n*-hexane (72 : 17 : 11) as an eluent (Sq PG = modified squalene with a pendant group or with a double-bond rearrangement). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with a Merck-Hitachi L-4000 UV detector. The UV detector was set at 273 nm, and the mobile phase was THF. Samples were prepared as follows: 0.1 g of the cold-quenched vulcanizate was dissolved in 10 mL of THF for 5 min in an ultrasonic bath at room temperature. Before injection, samples were filtered with a 0.45- μ m nylon filter to remove insoluble particles that would damage the column. The mobile phase flow was 1 mL/min, and the injection volume was 20 μ L. A Waters HR 0.5 Styragel column (Milford, MA) (7.8 \times 300 mm) was used.

RESULTS AND DISCUSSION

In a previous article submitted for publication by our group,¹⁶ we demonstrated that during micro-

wave-assisted squalene vulcanization, not only does the reaction take place in significantly less time, but the vulcanization is also more efficient. Such an effect is deduced from the fact that a higher percentage of disulfidic and monosulfidic bonds is formed compared to those obtained with conventional heating (calculated as the normalized area). Moreover, the role of the activator (ZnO) in the reaction is clearly less determinant when the heating is carried out with microwaves. Because of the important changes regarding reactivity observed when microwaves are involved, before the study of the effect of DPDS as a devulcanizing agent, it would be interesting to know the effect of microwaves on the reactivity of such a compound. Thus, in the mixture described in Table I, CBS was replaced by the same amount of DPDS.

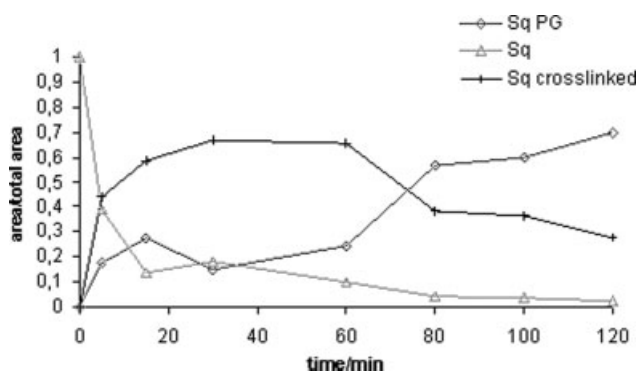


Figure 4 Squalene (Sq), crosslinked squalene (Sq crosslinked), and modified squalene (Sq PG) analyzed by HPLC-UV during the reaction with microwaves with 2 phr DPDS.

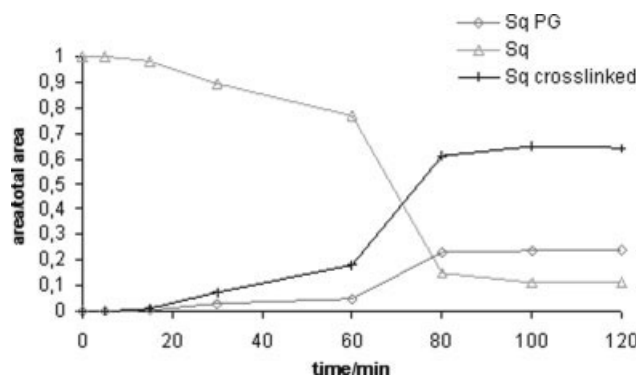


Figure 5 Squalene (Sq), crosslinked squalene (Sq crosslinked), and modified squalene (Sq PG) analyzed by HPLC-UV during the reaction with conventional heating with 2 phr DPDS.

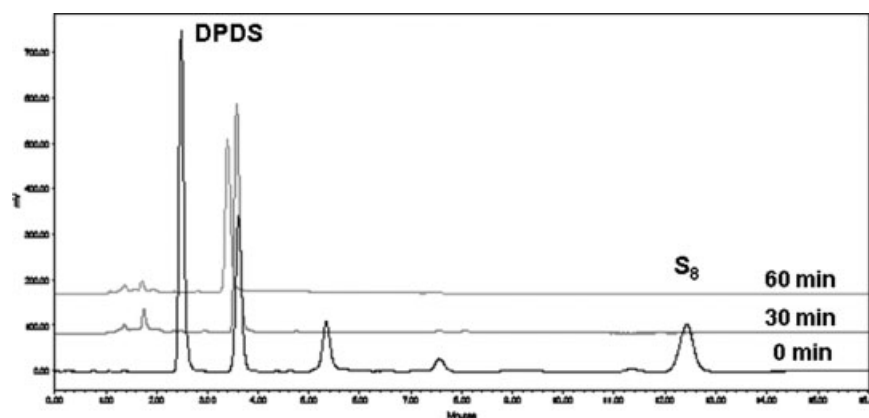


Figure 6 Evolution of DPDS by HPLC–UV during the reaction with microwaves.

The evolution of the squalene, crosslinked squalene, and squalene with a pendant group is presented in Figure 4 for the reaction carried out with microwaves and in Figure 5 for the reaction carried out with conventional heating for DPDS systems.

As can be seen, the crosslinking of squalene with DPDS occurs at 140°C in 5 min when microwaves are the heating system used. This crosslink formation was almost not detected for 30 min when the reaction was carried out with conventional heating at 140°C. During the second stage of the reaction, from minute 60 to 120, when the temperature is increased up to 200°C, the crosslinks that have formed with microwaves seem to be reversed. Such reversion was not observed for the crosslinked squalene obtained with conventional heating after 60 min at 200°C. It is a key point that the crosslink formation was obtained in a mixture that contained only DPDS and no other accelerator compound. The chromatograms corresponding to the evolution of DPDS under microwave heating at 0, 30, and 60 min are presented in Figure 6. Other peaks, identified as vulcanization intermediates, have been detected. Obvi-

ously this evolution was not observed when conventional heating was used.

The crosslinking effect of DPDS was compared with the vulcanization degree obtained with a conventional sulfenamide accelerator such as CBS. This was done by vulcanization of the reaction mixture with both microwaves and conventional heating with the formulation described in Table I. The results obtained regarding the vulcanization degree compared with those obtained with DPDS are presented in Figure 7. As can be seen, the crosslink degree achieved with DPDS heated with microwaves was almost the same as that corresponding to CBS. To explain this ability of DPDS to behave as a good accelerator at 140°C when microwaves are used, an experiment of vulcanizing a recipe without an accelerator was performed (squalene, ZnO, stearic acid, and sulfur). It can be observed that microwaves allow the sulfur reaction with the polymer chain with good kinetics. The presence of DPDS gives more control of the sulfur transfer to the polymer chain because of the ability of DPDS to form intermediates similar to the active sulfurating agents formed by conventional accelerators such as CBS.

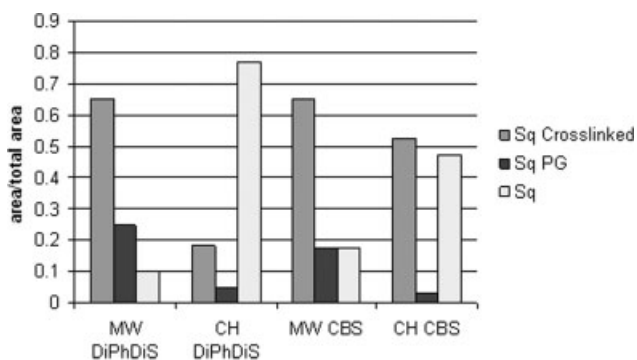


Figure 7 Comparison of the vulcanization degree obtained after 60 min at 140°C with both heating systems with CBS and with DPDS (MW = microwaves; CH = conventional heating; Sq = squalene; Sq crosslinked = crosslinked squalene; Sq PG = modified squalene).

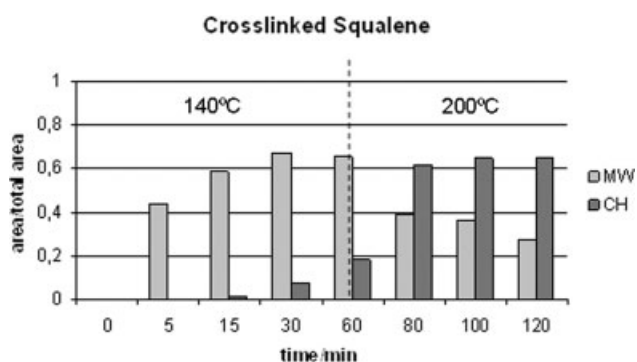


Figure 8 Evolution of crosslinked squalene with both heating systems and DPDS (MW = microwaves; CH = conventional heating).

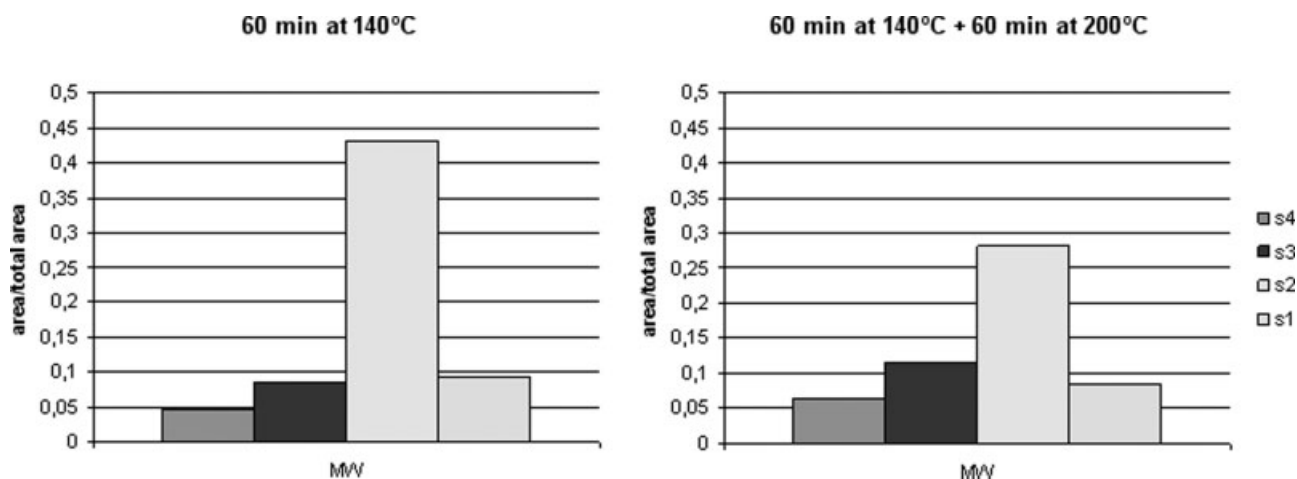


Figure 9 Influence of the DPDS treatment on different types of polysulfidic crosslinks.

Nevertheless, conventional heating allowed an acceptable crosslink degree only when CBS was used. That means that the presence of sulfur is necessary at 140°C to allow DPDS to behave as an accelerator. This compound by itself is active only up to 180°C when the disulfidic bond cleavage starts. This can be supported by the fact that when a mixture of CBS and DPDS was heated with microwaves at 140°C, only CBS reacted, DPDS remaining unchanged during the reaction.

However, the interest in DPDS is due to its ability to produce devulcanization.⁴ To bring some insight into this aspect, it is important to study the behavior of the mixtures after heating with both microwaves and conventional heating at 200°C. In Figure 8, the crosslinked squalene evolution is presented after 60 min at 200°C with both heating methods. It seems that at 200°C with microwaves, the crosslinks decreased significantly. In Figure 9, it can be seen that despite the known stability of disulfidic crosslinks, these are the most affected by the treatment developed (Fig. 9) because the microwave energy is

sufficient to cleave the disulfide crosslink bonds. On the other hand, the use of conventional heating under such conditions did not show any significant devulcanization. Moreover, the temperature increase led to the formation of more crosslinks. When the squalene was vulcanized with CBS in the absence of DPDS and then heated with microwaves at 200°C for 60 min (Fig. 10), no significant changes were observed in the number of crosslinks formed. This confirms that the observed devulcanization is a result of the combination of DPDS with microwaves.

The use of GPC to follow the reaction allowed us to confirm that the devulcanization effect of DPDS leads to the formation of a pendant group in the squalene chain. This means that the devulcanizing agent reacted with the sulfidic bonds through a radical mechanism,³ breaking the crosslinks and remaining attached to the main chain (Fig. 11 and Scheme 1).

A final question to be answered is if it is possible to control the DPDS reactivity by a change in the reaction temperature. In Figure 12, the evolution of

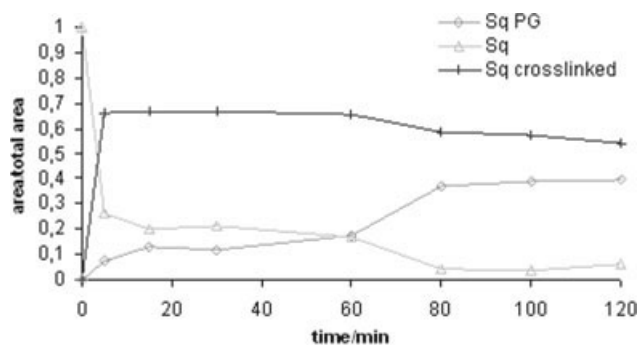


Figure 10 Evolution of squalene (Sq) crosslinks (vulcanization with CBS) after 120 min of microwave heating at 200°C in the absence of DPDS (Sq crosslinked = crosslinked squalene; Sq PG = modified squalene).

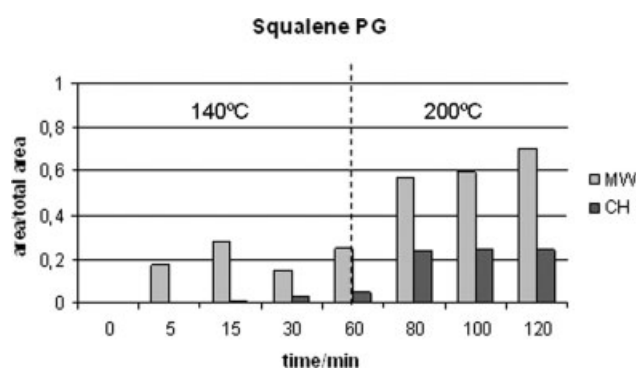
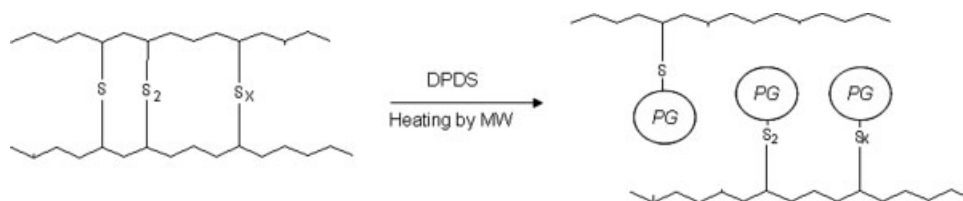


Figure 11 Evolution of squalene with a pendant group (PG) during the microwave heating of a mixture with only DPDS (MW = microwaves; CH = conventional heating).



Scheme 1 Pendant group (PG) formation (MW = microwaves).

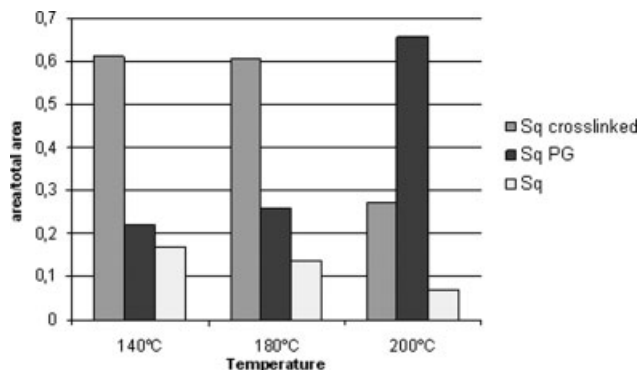


Figure 12 Comparison of the amounts of squalene (Sq), crosslinked squalene (Sq crosslinked), and squalene with a pendant group (Sq PG) for samples treated with microwaves at 140, 180, and 200°C for 60 min.

crosslinked squalene and squalene with a pendant group at three different temperatures (140, 180, and 200°C) is shown. It can be clearly seen that the devulcanization reaction occurred only when the temperature reached 200°C. This could be important in industrial devulcanizations because it seems possible to tune the process by the choice of the proper temperature for the treatment.

CONCLUSIONS

The efficiency of microwaves heating in a devulcanization process with DPDS as a devulcanizing agent has been proved with an MC vulcanization approach. The reaction can be tuned through the temperature setting and microwave power control. Thus, it is possible to introduce DPDS during com-

pounding and activate its devulcanizing ability by control of the temperature and power of the microwaves when required.

The devulcanization mechanism seems to lead to the final formation of a pendant group of the devulcanizing agent on the squalene chain.

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