Vulcanization of Polybutadiene Rubber with Dipentamethylene Thiuram Tetrasulfide

P. Posadas, A. Fernández, J. Brasero, J. L. Valentín, A. Marcos, A. Rodríguez, L. González

Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cieva 3, 28006 Madrid, Spain

ABSTRACT: The cure of polybutadiene rubber (BR) with sulfur donor dipentamethylene thiuram tetrasulfide (DPTT) does not show reversion reaction, in contrast with similar natural rubber compounds. No polysulfure links are formed; whereas a great amount of —C—C— crosslinks are produced. The addition of tetramethyl thiuram monosulfidic (TMTM) strongly affects the crosslinking process. Mechanical properties of the cured compounds are poor. In DPTT, curing of BR the radical species produced through homolitic cleavage of DPTT molecule seems to have sufficient energy to produce crosslinking, via allylic abstraction, and also initiate the polymerization of double bonds producing areas of high crosslinking density that induce early material failure. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3481–3487, 2007

Key words: elastomers; networks; crosslinking; physical properties

INTRODUCTION

A great amount of information on the nature of the sulfur vulcanization has been achieved since its discovery in the 19th century. However, important research effort continues today towards understanding this complex chemical process. The mechanism of accelerated sulfur vulcanization remains undisclosed and essential aspects about curing are even unknown.

In practice, three stages in the process of vulcanization are considered. The first one involves the "accelerator chemistry" where the reactions lead to the formation of an active sulfurating agent. A second stage corresponds to the "chemistry of crosslinking," which includes reactions leading to the formation of crosslink and finally the "post crosslinking chemistry," which involves reactions of shortening and degradation of crosslinks.[1]

The first step, in vulcanization systems accelerator/sulfur, begins with the formation of an active accelerator complex via reaction of the accelerator and activators, which subsequently reacts with molecular sulfur to form the sulfurant species that then react preferentially with an allylic carbon. This crosslink precursor then reacts with an additional allylic carbon of another rubber chain, with the result of a polysulfidic crosslink.

The present work is the continuation of the study on the vulcanization with sulfur donors, where the natural rubber was vulcanized with dipentamethylene thiuram tetrasulfide (DPTT).[2,3] The network obtained presented a homogeneous distribution of the crosslinks, and the compounds presented high values of tensile strength. The chemical crosslinks structure was of three types: polysulfidic, disulfidic, and monosulfidic, with the polysulfidic structures being the most abundant species, around 70%.

In this context the purpose of this article is to continue the study of the vulcanization with polybutadiene rubber and the same sulfurating agent, DPTT. No sulfur was added to the formulation, and zinc oxide and stearic acid were included as activators or omitted.

EXPERIMENTAL

Materials

The polybutadiene rubber used was Intene 50, consisting of 98% by weight of 1,4 cis polymer. The other compound ingredients used were extra pure grade zinc oxide, 95% pure stearic acid, dipentamethylene thiuram tetrasulfide (DPTT), and tetramethyl thiuram monosulfide (TMTM).

Blending and curing

The master batches were compounded on a two roll-mill, at a temperature of 40–50°C. Measurements of

the grade of curing were conducted in a Monsanto Moving Die Rheometer, Mod. MDR 2000 E. All samples were cured at optimal cure time t_{97} in the form of 2-mm thick sheets in a thermo-fluid heated press.

Physical testing

Tensile strength tests were performed at room temperature on an Instron Tensile Tester, Mod 4301, with grip separation speed of 50 cm/min. The test samples were cut out from the vulcanized sheets using a microtensile dumbell-type die. All tensile results reported are the average values of five tests.

Determination of density, type, and distribution of crosslinks

The concentration of crosslinks was determined from equilibrium swelling data. Vulcanizate samples weighing 0.2–0.3 g were allowed to swell in toluene containing 0.1% phenyl-β-naphthyl amine. After equilibrium was attained, the swollen sample was weighed, the solvent removed in vacuum and weighed again. The volume fraction of rubber in the solvent swollen network was then calculated by the method reported by Ellis and Walding.[4] The crosslink density was determined using the Flory-Rehner equation.[5]

The concentration of polysulfidic crosslinks was estimated from the change in the crosslink density of the vulcanizates before and after treatment with 0.2M solution of propane-2-thiol dissolved in piperidine for 6 h, which cleaves only the polysulfidic crosslinks in the network.[6–8] The volume fraction of rubber and the crosslink density after cleavage were determined as previously explained.

Both polysulfidic and disulfidic crosslinks in the vulcanizates could be cleaved by treatment with 1-hexane-thiol 1M in piperidine for 48 h at 25°C.

Determination of chemical crosslinks concentration, before and after treatment with each of these reagents, allows the calculation of the individual contribution of poly-, di-, and mono-sulfidic (plus —C—C—) crosslinks to the total degree of crosslinks.

Also, the vulcanizates were treated with methyl iodide in mild conditions to break the monosulfidic crosslinks. After the degradations of the poly- and di-sulfidic crosslinks, the samples were treated with methyl iodide to discriminate —C—C— linkages from monosulfidic linkages.[9]

THEORY

The controversy on the nature of the action of the active sulfurating agents remains. In absence or presence of zinc oxide and stearic acid a free radical mechanism,[8–10] in which the active sulfurating agent is an accelerant polysulphide, seems to fit the experimental results best. The thermal scission of DPTT is proposed to take place through homolitic cleavage to produce radical species as shown in scheme [1]

[1]
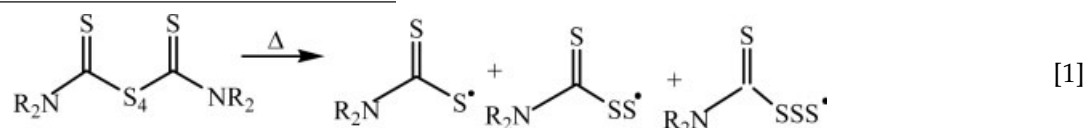
The unsymmetrical cleavage is also possible; however, it is not so likely, since it requires breaking of the more stable C—S bond.

A variety of exchange reactions can occur in the early stages of vulcanization. Gradwell and

McGill[11] suggest exchange reactions between the radical species indicated in [1] with DPTT to obtain radicals of higher sulfur rank, as shown in scheme [2]


[2]
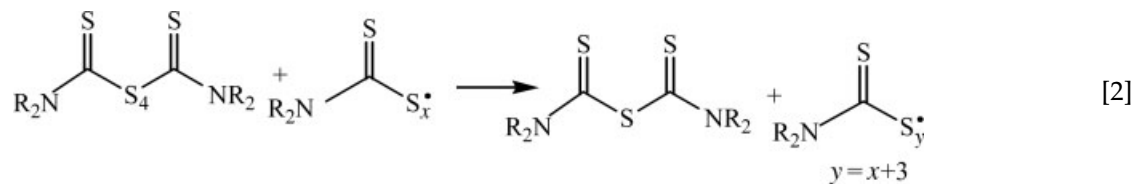
Also, the formation of this sulfurant products can occur via the recombination of radicals,[12,13] because the result obtained requires that the exchange reaction can be generalized to include longer polysulfidic species. In general, for these

reactions to occur, the intermediate free radical must have sufficient stability so that it can diffuse in the matrix and react to form species with higher sulfur rank. The stability of this radical species is due to resonance stabilization and formation of a

three-electron bond between the two terminal sulfur atoms.[14,15]

The thiocarbonyl radical indicated in [1], or others obtained via recombination of radical species, can

abstract a hydrogen atom of the rubber to form the crosslink precursor or sulfurating agent. This species subsequently reacts with another rubber molecule through the same free radical pathway to form a crosslink


[3]
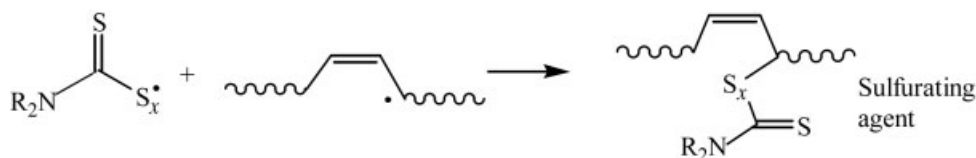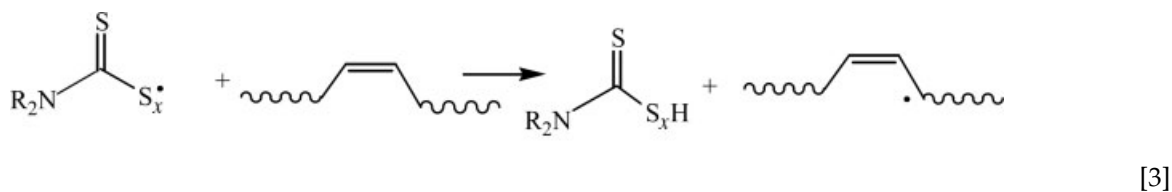
Also, the recombination of two macroradicals can form a crosslink. Even though this may be chemically plausi-

ble, the limited diffusional mobility of two macroradicals indicates that such a reaction would be unlikely

[4]
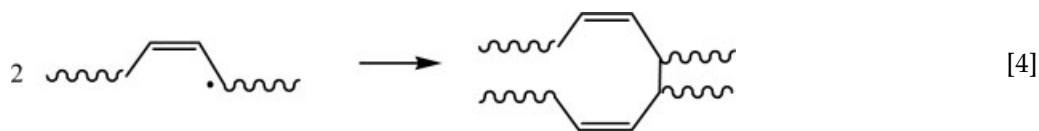
This active sulfurating species can also be transformed in to a crosslink via disproportionation. In this case, two
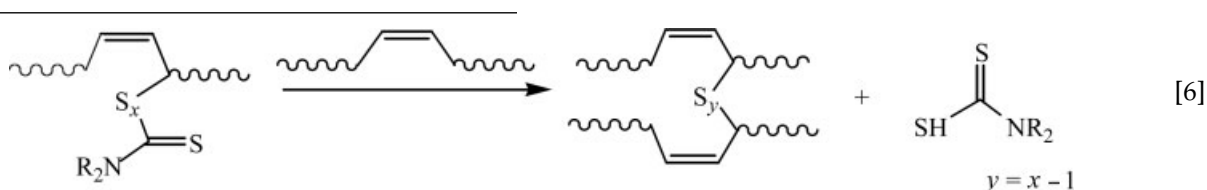
crosslink precursors form one crosslink and an accelerator polysulfide

[5]

$$2x = y + z$$
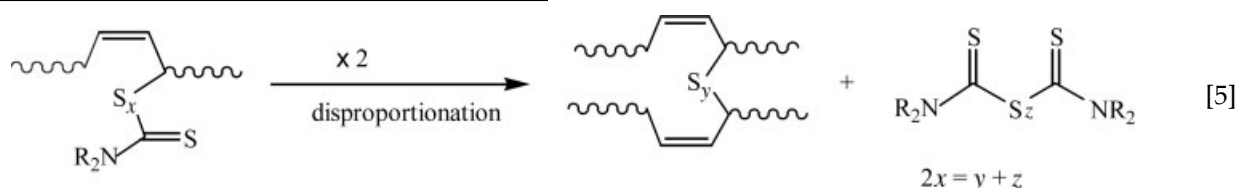
With this reaction of disproportion it is possible to obtain also the formation of crosslink of higher lengths. However, the reaction cannot account for the formation of monosulfidic crosslink. Another objection comes from the consideration of the low diffusional mobility, as we are dealing with bulky molecules which must diffuse in a

highly viscous rubber matrix. The formation of crosslink by this mechanism is probably not very important.

Another possible mechanism of formation of a crosslink is by direct reaction of the crosslink precursors with an allylic moiety of a near rubber chain,[16,17] as given in [6]


[6]

$$y = x - 1$$

The reaction is assumed to proceed by a radical mechanism where the crosslink precursor splits into two active radicals, a persulfonyl polymeric radical, which can react with an allylic carbon on a neighbouring isoprene chain and thus form a crosslink, and other polysulfidic radical, which can undergo a variety of reactions like radical combination to yield more accelerator polysulfidic species, or also addition to a new rubber chain to form another crosslink precursor.

In general, it is necessary to emphasize the importance of the free radical reaction between the different accelerator species in the absence of sulfur. Specially, for these reactions to occur, the free radical intermediates must have sufficient stability so that they can diffuse and react to form the polysulfidic species. Evidence of the existence of radical species is provided by EPR spectroscopy.[18,19] It is possible to conclude that the rubber vulcanization proceed via radical intermediates, however, a mixed radical and polar mechanism results upon addition of zinc oxide to system.

Since the concentration of allylic hydrogen in the isoprene chains (seven allylic hydrogen for monomer unit) is higher than the concentration of any other polysulfidic reactive species, it seems more probable that the polysulfidic radical species react first with allylic hydrogen in the elastomer backbone. However, since in the polybutadiene rubber the allylic hydrogen concentration is lower (four allylic hydrogen for monomer unit); it is also possible to have an increasing probability for the radical polysulfidic species to react with the double bond of the butadiene units with the incorporation of the accelerator moiety into the rubber structure, followed by a "polymerization."[20]

[7]
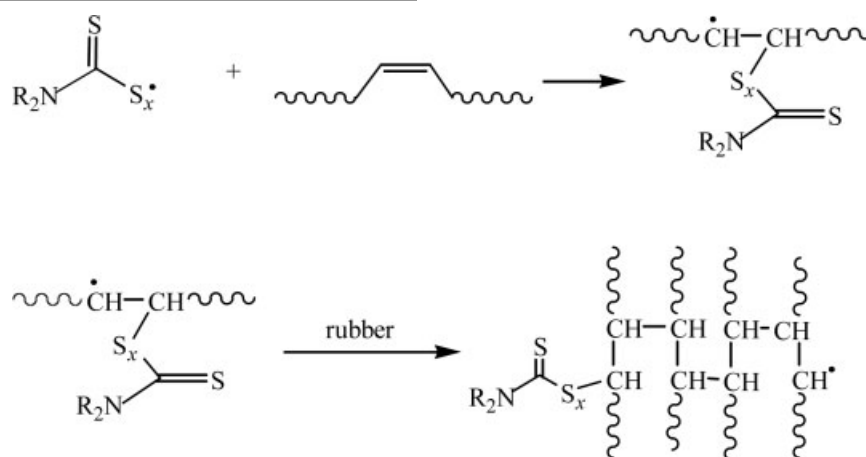
Polysulfidic radical indicated in [1] can react with the butadiene double bond of rubber producing also a "polymerization" reaction, which generates small cluster of densely crosslinked polymer.

Coran[16,17] and Coleman et al.[18] found that the addition of activators zinc oxide and stearic acid does not fundamentally alter the mechanism of sulfuration. The presence of the activator should merely increase the rate of reaction but not affect the basic trends in the product distribution.

RESULTS AND DISCUSSION

Table I shows the formulations for the polybutadiene rubber with DPTT, with or without activators zinc oxide/stearic acid. The crosslinking process was measured with an oscillating die rheometer. The rheograms of the compound C2, which contains activator agents, at different temperatures, are show in Figure 1. At the three temperatures of the compound displays a flat plateau indicating that the

formed crosslinks are thermally stable, and therefore, the unstable sulfur structure ($-S_{x>2}-$) must be almost absent in the rubber network. This behavior is surprising, as it was expected that this compound cured at 160°C would show some reversion. A similar compound with natural rubber as base rubber[2,3] showed reversion. The absence of reversion was measured during 120 min.

The maximum torque increases with DPTT concentration, and the cure data obtained for the compounds at 150°C are given in Table II. The optimum

TABLE I
Compounds Formulations, (phr)

Compound	C1	C2	C3	C4	C5	C6
BR (Intene 50)	100	100	100	100	100	100
Zinc oxide	5	5	5	–	5	5
Stearic acid	1	1	1	–	1	1
DPTT	2	3	4	2	3	–
TMTM	–	–	–	–	3	3

Figure 1 Rheometer curves for compound C2 cured at 150°C (●), 160°C (○) and 170°C (▼).
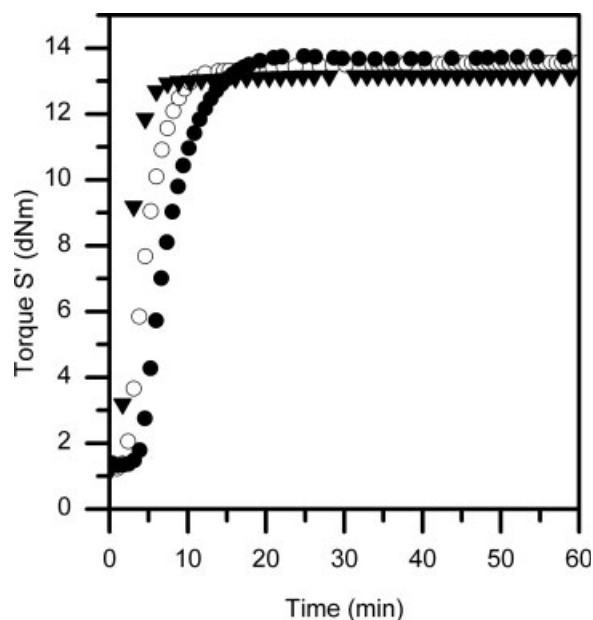

Figure 2 Rheometer curves for compound C4 cured at 150°C (●), 160°C (○) and 170°C (▼).

cure time (t_{97}) decreases with the addition of DPTT. In all cases the reversion reaction was null, in great contrast with the strong reversion found in NR formulations.[2,3]

The response of compound C4 with the same content of DPTT as C1 but without ZnO/stearic acid is represented in Figure 2. It must be noted that the formulation with ZnO shows an increase in the rate of reaction of crosslinking as well as in the maximum torque. This response implies that for compounds cured with DPTT and activator agents, the crosslink density is much higher than in the case without activator. It agrees with other reported research work, the presence of ZnO increases not only the rate of reaction but also the distribution and crosslinks density.[1]

Table III shows the variation in crosslink density for different compounds vulcanized at 150°C for their optimum times, measured by equilibrium swelling in toluene and calculated with Flory-Rehner method. For the C1, C2, and C3 compounds, with different levels of DPTT, the crosslink density progress in linear form. With respect to crosslink types, the polysulfidic species are not present and the di-
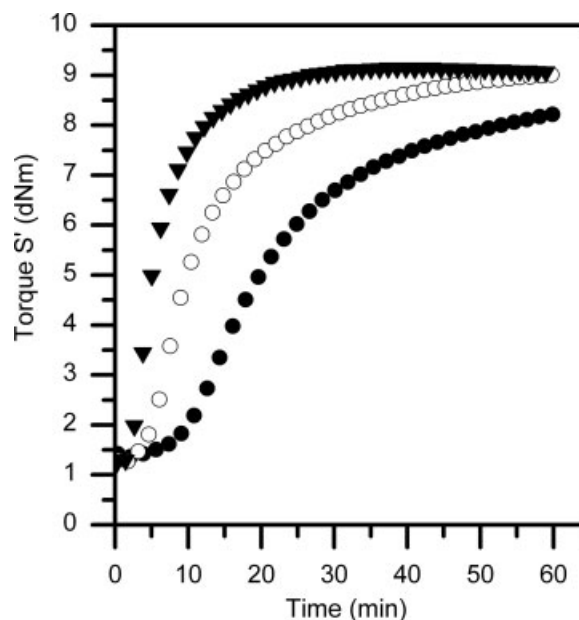
and mono-sulfidic crosslinks are present in similar relative content. Because of the absence of $-S_{x>2}-$ species, both the reaction between the radical species (obtained from the thermal cleavage of DPTT given in [1]) to obtain species with higher sulfur rank [2], and the route of disproportionation seems to be no present. It is possible to assume that the indicated thiocarbonyl radical species form the crosslink precursor by direct reaction with an allylic moiety, and then a crosslink via allylic substitution, shown in [4]. However, the presence of $-C-C-$ crosslink was not expected, and their content is $\sim$ 50% of the total crosslinks content. This result can be attributed to the fact that during curing process the polysulfidic radical's species [1] can initiate a polymerization reaction with double bonds between adjacent chains, as shown in [7]. This model implies the consideration of zones with high crosslink density (cluster) or junctions of elevated functionality.

Figure 3 shows the changes in crosslink density for compounds cured with different DPTT concentration. The variation is linear with the proportion of sulfur donor. The theoretical curve corresponds to density crosslink obtained if the two useful sulfur atoms per DPTT molecule participate only as monosulfidic structures. This statement allow us to corroborate that the contribution of the additional reaction of the persulfonyl radicals to double bonds may give rise to a polymerization between adjacent double bonds generating a network with a more complex texture, and inhomogeneous crosslink distribution.

When the process of vulcanization with DPTT is carried out in presence of TMTM, the crosslinking process is strongly affected. The sample C5 similar

TABLE II
Rheometer Data for Compounds at 150°C

Compound	C1	C2	C3	C4	C5
Optimum cure t_{97}, min	17.5	11.9	9.1	51.2	25.6
T_{max}, (dNm)	11.6	13.6	15.4	9.1	16.3
ΔT, (dNm)	10.4	12.4	14.2	8.0	15.2
Reversion[a]	null	null	null	null	null

[a] $(T_{max} - T_{120'})/(T_{max} - T_{min}) \times 100$.

TABLE III
Distribution of Different Crosslink Type for Compounds Cured at 150°C for Their Optimum Cure Time

Compound	C1	C2	C3	C4	C5
Crosslink density, (mole/cm^3 × 10^4)	2.0	2.55	3.01	0.85	3.28
Total polysulfure, $S_{x>2}$, (%)	0	0	0	0	3.7
Total disulfure, S_2, (%)	21	22	26	92	2
Total monosulfure, S_1, (%)	24	26	25	Dissolved	78
Total —C—C—, (%)	55	52	49	–	17

to C2, with addition of 3 parts per hundred of rubber (phr) of TMTM is added, the optimum cure time and maximum torque increased with the presence of this second accelerant. In sample C5, the distribution of the several types of crosslink is different to the distribution of the rest of compounds. The relative content of monosulfidic links is higher than for the rest of the compounds.

Thermal scission of TMTM give radical species $R_2NC(=S)S^\bullet$ and $R_2NC(=S)^\bullet$, none existing the possibility of exchange reactions that form radicals of higher sulphur rank. The compound C6, with only TMTM and activators, cured at 150°C, not forming crosslink in the absence of sulphur; the torque increment being negligible. The two radicals obtained from thermal scission cannot react with the rubber and form crosslinks. These results allow us to assume that between the radical species shown in [1], only the persulfonyl radical could initiate the crosslink reaction. The species $R_2NC(=S)S^\bullet$ cannot react with the allylic hydrogen in the polybutadiene chain. However, when TMTM is incorporated to compounds cured with DPTT (compound C5), the

maximum torque, the crosslink density, and the distribution of crosslink types, were strongly modified.

Table IV gives the physical properties of the compounds cured at 150°C and their optimum times. The shore A hardness increases proportionally with DPTT concentration, an indication of networks with higher crosslink density. The tensile strengths are very low. This important drop can be explained by the fact that, during crosslinking, the persulfonyl radical species react with rubber by addition to double bonds. This mechanism would give rise to relatively small volumes of densely crosslinked polymer (clusters). When the heterogeneous networks are subjected to strain, the nonuniform stress distribution may induce anticipated material rupture.

When a radical is generated by peroxide decomposition in presence of diene rubbers, in addition to abstraction of a hydrogen atom in allylic position, it can attach to a double bond and give rise to intermolecular polymerization between double bonds of different chains. The crosslinking efficiency for the vulcanisation of natural rubber with dicumyl peroxide is only slightly above unity. However, in styrene-butadiene and polybutadiene elastomers it has been observed to be 10 or more. These differences show that the polymer structure is an important factor in the competition between hydrogen abstraction and addition reactions. This might be due, at least in part, by steric considerations. In butadiene-based rubbers, the double bonds are quite accessible, with minor steric hindrance, while in the case of isoprene rubber the methyl group can act as a shield for the double bonds minimising the addition reaction.

When the mechanism of vulcanization of natural rubber with thiuram sulfur donors[2,3] is examined, the crosslink formation proceeds via disproportionation preferentially, with significant amount of polysulfidic crosslinks, minor proportion of disulfidic
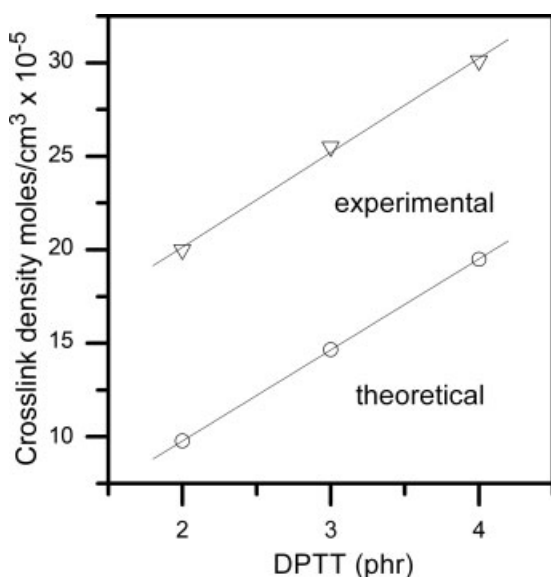

Figure 3 Changes in crosslink density for compounds with different content in DPTT. Theoretical line corresponds to entirely monosulfidic structures.

TABLE IV
Physical Properties of Compounds Cured at 150°C for Their Optimum Cure Time

Compound	C1	C2	C3	C4	C5
Hardness (Shore A)	44	51	53.5	41	56
Tensile strength, (MPa)	1.2	1.3	1.4	1.2	1.1
Elongation at break (%)	150	105	105	210	105

links, and only testimonial content in S_1 + —C—C—. However, when the process of vulcanization of polybutadiene elastomers with DPTT is examined, the polysulfidic species are not present, the route of disproportionation seems to be absent, and the di- and monosulfidic crosslinks are present in similar relative content, with the surprising presence of —C—C— crosslinks in $\sim 50\%$ of total crosslink content. The radical species produced through homolitic cleavage of DPTT molecule, shown in [1], can initiate the addition reaction [7]. These results are similar to those obtained with dicumyl peroxide. The polysulfidic radical species seems to have sufficient energy to produce addition reaction with the polybutadiene rubbers, with incorporation of the initiating radical fragment into the polymer matrix, while due to steric hindrance, in natural rubber this radical species are scarcely accessible to double bonds.

CONCLUSIONS

The cure of BR with the sulfur donor DPTT, with or without the presence of activator zinc oxide/stearic acid does not show signs of reversion, in great contrast with previous finding for NR.

Presence of activator increases the maximum torque reached, and also the increase in DPTT content in the formulation. No polysulfur links are formed whereas a great amount of —C—C— bonds are produced. The addition of monosulfide TMTM strongly affects the crosslinking process, with some polysulfur link formed, and monosulfur species as the main type of crosslink produced.

Mechanical properties of the cure compounds are poor. These results are interpreted in terms of the crosslinking mechanism. In DPTT curing, only per-

sulfenil radicals seem to be able to produce crosslinking, via allylic abstraction, with disproportionation completely absent, and at the same time this radical can initiate the polymerization of double bonds in neighboring chains producing areas of high crosslinking density that induce early material failure.

References

1. Ghosh, P.; Katare, S.; Patkar, P.; Cathers, J. M.; Venkatasubramanian, V.; Walker, K. A. Rubber Chem Technol 2000, 76, 592.
2. González, L.; Rodríguez, A.; del Campo, A.; Marcos-Fernández, A. Rubber Chem Technol 2000, 73, 89.
3. González, L.; Rodríguez, A.; del Campo, A.; Marcos-Fernández, A. J Appl Polym Sci 2002, 85, 491.
4. Ellis, B.; Walding, G. N. Soc Chem Ind 1963, monogralpf 17, 46.
5. Flory, P.; Rehner, J. J Chem Phys 1943, 11, 521.
6. Saville, B.; Waston, A. A. Rubber Chem Technol 1967, 40, 100.
7. Campbell, D. S. J Appl Polym Sci 1969, 13, 1201.
8. Coleman, M. M.; Shelton, J. R.; Koening, J. L. IEC Prod Res Dev 1973, 46, 957.
9. Shotman, A. H. M.; van Haeren, P. J. C.; Weber, A. J. M.; van Wijk, F. G. H.; Hofstraat, J. W.; Talma, A. G.; Steembergen, A. Rubber Chem Technol 1996, 69, 727.
10. Kruger, W. H.; McGill, W. J. J Appl Polym Sci 1992, 45, 573.
11. Gradwell, M. H. S.; McGill, W. J. J Appl Polym Sci 1994, 51, 169 and 51, 177.
12. Gradwell, M. H. S.; Hendrikse, K. G.; McGill, W. J. J Appl Polym Sci 1995, 56, 1581.
13. Kapur, R. S.; Koening, J. L.; Shelton, J. R. Rubber Chem Technol 1974, 47, 911.
14. Fairbrother, F.; Gee, G.; Merral, G. T. J Polym Sci 1955, 16, 459.
15. Triette, C. D.; Morita, J. E.; Young, E. J. J Appl Polym Sci 1962, 35, 1360.
16. Coran, A. Y. Rubber Chem Technol 1964, 37, 673, 679.
17. Coran, A. Y. Rubber Chem Technol 1965, 38, 1.
18. Coleman, M. M.; Shelton, J. R.; Koening, J. L. Rubber Chem Technol 1973, 46, 938.
19. Shelton, J. R.; Mc Donel, E. T. Rubber Chem Technol 1960, 33, 342.
20. Van Hoff, B. M. E. Appl Polym Symp 1968, 7, 2.