Crosslink Reaction of Natural Rubber with Thiuram Sulphur Donors in the Presence of a Thiuram Monosulfide

L. GONZÁLEZ, A. RODRÍGUEZ, A. DEL CAMPO, A. MARCOS-FERNÁNDEZ

Instituto De Ciencia y Tecnología de Polímeros (CSIC), C/ Juan de la Cierva, 3-28006 Madrid, Spain

ABSTRACT: The vulcanization of natural rubber was studied with the sulfurating agents dipentamethylene thiuram tetrasulfide (DPTT) and tetramethylene thiuram disulfide (TMTD) in the presence of tetramethyl thiuram monosulfide (TMTM). This last accelerant affects the rate and efficiency of the vulcanization as well as the structures of crosslinks formed by the two sulphur donors. It may give rise to a polymerization between adjacent double bonds and generate a inhomogeneous crosslink distribution with an adverse effect on physical properties. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 491–499, 2002

Key words: rubber; crosslinking; networks; mechanical properties

INTRODUCTION

The vulcanization of natural rubber (NR) was examined with the sulfurating agents dipentamethylene thiuram tetrasulfide (DPTT) and tetramethylene thiuram disulfide (TMTD). These sulfurating agents react with the rubber chain to form C—S bonds. Throughout, no sulphur was added to the formulations, and ZnO and stearic acid were included as activators.

These sulfurating agents present the three reaction stages of vulcanization: formation of rubber bonded intermediates, their conversion to crosslink, and crosslink shortening. The presence of ZnO catalyzes the formation of the sulfurating agent and improves the crosslinking efficiency.[1–5]

This article is the continuation of the study on the vulcanization with sulphur donors.[6] A thiuram monosulfide (TMTM) was included in the formulations. This accelerant can affect the rate and efficiency of the vulcanization as well as the structures of the crosslinks formed by these two sulphur donors, DPTT and TMTD.

EXPERIMENTAL

Materials

All compounds are based on standarized NR (NR SMR), provided by Seng Hin Rubber (M) SDN BHD (Malaysia).

Crosslinking was affected using dipentamethylene thiuram tetrasulfide (DPTT), tetramethyl thiuram disulfide (TMTD), and tetramethyl thiuram monosulfide (TMTM), provided by Flexsys NV (Brussels, Belgium).

Blending and Curing

The master batches were compounded on a two-roll mill, at a temperature of 40–50°C. Measurements of the degree of curing were conducted in a Monsanto Moving Die Rheometer, Model MDR 2000E. All samples were cured in a thermo-fluid heated press.

Table I   Compound Formulations[a]

Compound	1	2	3	4
NR	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	1	1	1	1
TMTD	4	—	4	4
TMTM	—	4	4	8

[a] Formulations given as phr, parts per hundred parts of rubber.

Physical Testing

Tensile strength tests were performed at room temperature on an Instron Tensile Tester, Model 4301, with a 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 the Density, Type and Distribution of Crosslinks

The concentration of crosslinks was determined from the equilibrium swelling data. Vulcanizate samples weighing 0.2–0.3 g were allowed to swell in toluene containing 0.1% phenyl-β-naphthyl amine (PBN). After equilibrium was attained, the swollen sample was weighed, the solvent removed in vacuum and weighed again. The volume fraction of rubber (Vr) in the solvent swollen network was then calculated by the method reported by Ellis and Welding.[7] The crosslink density was determined using the Flory–Rehner equation.[8]

The concentration of polysulphidic crosslinks was estimated from the change in the crosslink density of the vulcanizates before and after treatment with 0.2 M solution of propane-2-thiol dissolved in piperidine for 6 h, which cleaves only to the polysulphidic crosslinks in the network.[9,10] The volume fraction of rubber and the crosslink density were determined as previously explained.

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

Determination of the chemical crosslinks concentration, before and after treatment with each of these reagents, allows the calculation of the individual contribution of mono-, di-, and poly- sulphidic crosslinks to the total degree of crosslinks.

Two vulcanized compounds were treated with methyl iodide in mild conditions in order to break the monosulfidic crosslinks while keeping the di- and poly- sulphidic crosslinks intact. In this way, the existing carbon—carbon crosslinks present in the vulcanizate can be determined.

RESULTS AND DISCUSSION

Crosslink Reaction of NR with TMTD in the Presence of TMTM

In the presence or absence of zinc oxide, evidence exists that supports a predominantly free-radical mechanism (Coleman et al.[11,12] and Coran[13,14]). The thermal degradation of TMTD is proposed to take place through a reversible homolytic scission:
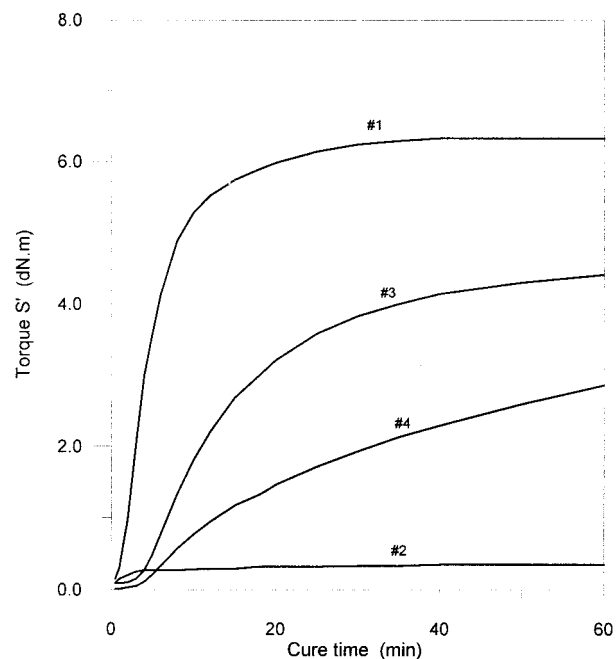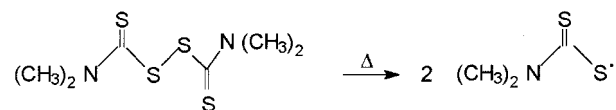

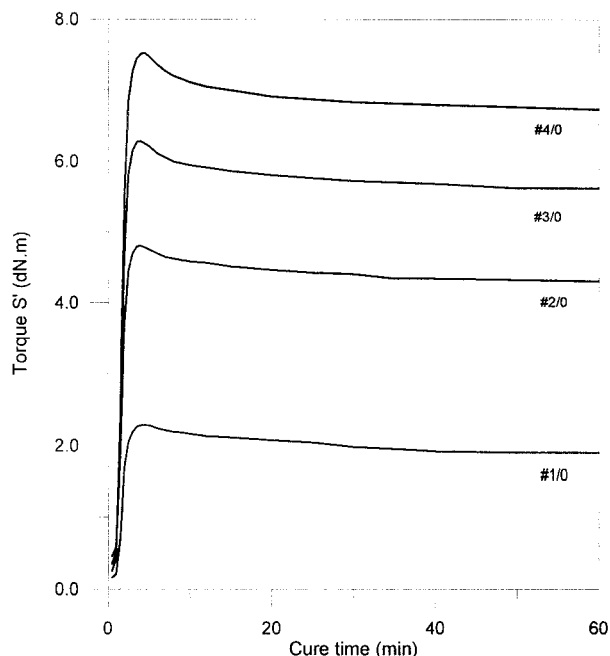**Figure 1**   Rheometer curves for compounds 1, 2 and 3 cured at 150°C.

Figure 2 Rheometer curves for compounds with different DPTT levels without TMTM.

The asymmetric scission with formation of $Me_2NC(=S)^\bullet$ and $Me_2NC(=S)SS^\bullet$ radicals would appear to be unlikely due to the great stability of the C—S bond in comparison with the S—S bond.[15]

The monosulphenyl radical can abstract an allylic hydrogen atom from the rubber chain:
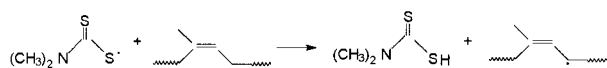
And this polymeric radical can react with another monosulphenil radical:

This species constitutes the crosslink precursor or sulphurating agent.
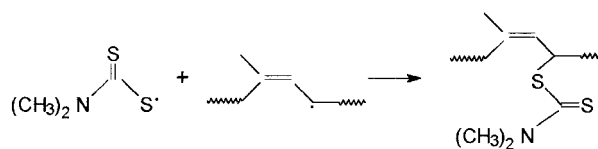
This process of crosslink formation with TMTD compounds demonstrated[6] that the structure of the chemical crosslink produced during vulcanization was mainly —S—S—, with approximately 70% relative content, and the rest being —S—. This result for TMTD compounds cannot be attained by allylic substitution or by dispropotionation. Another mechanism was proposed to account for the disulphidic crosslink, in which the sulphurating agent can undergo disproportion with unreacted TMTD.

When heating TMTD in the presence of TMTM, the crosslink formation is strongly affected. Table I shows the formulations for the natural rubber compounds with TMTD, zinc oxide and stearic acid, with or without the presence of TMTM. The crosslinking process was measured with an oscillating die rheometer. The rheograms of the different compounds at 150°C are shown in Figure 1. The development of the crosslink reaction of compound 1 is typical: induction and curing times are very short, reversion phenomenon is not detectable, and the vulcanization reaction adjusts to a first-order reaction. Compound 2, with TMTM, is unable to form crosslinks, and the torque increment is negligible. Compounds 3 and 4 show an important reduction in torque with respect to compound 1, and this diminution is dependent on TMTM content.

This behavior of TMTM, not forming crosslinks in the absence of sulphur, cannot be satisfactorily explained with previous arguments.[6]

An asymmetric scission[11] is probable when heating TMTM, which leads to $Me_2NC(=S)S^\bullet$ and $Me_2N(C=S)^\bullet$. The latter radical can react

Table II   Compound Formulations[a]

Compound	1/0	1/1	2/0	2/1	2/2	3/0	3/1	3/2	3/3	3/4	3/6	3/8	4/0	4/4
NR	100	100	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1	1	1	1	1	1	1
DPTT	1	1	2	2	2	3	3	3	3	3	3	3	4	4
TMTM	—	1	—	1	2	—	1	2	3	4	6	8	—	4

[a] Formulations given as phr.

with the monosulphenyl radical produced on the decomposition of TMTD:
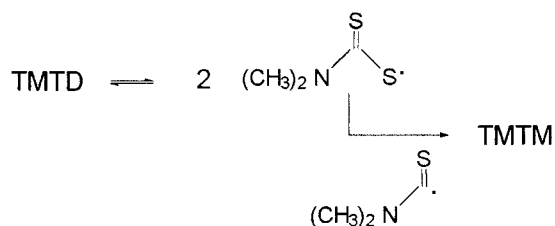
The carbonyl radical generated in the asymmetric scission of TMTM can recombinate with the monosulphenyl radical generated on the scission of TMTD, but because a TMTM molecule generates the same amount of monosulphenyl radical as it substracts by recombination, the overall monosulphenyl radical production would be the same (for TMTM content equal or below TMTD content). No differences should be found on the TMTD curing with or without the presence of TMTM.

If the crosslinking mechanism is examined, admitting the formation of the sulfurating agent, an allylic substitution was ruled out[6] because it could not lead to crosslinking with TMTD. Disproportionation between sulfurating agents
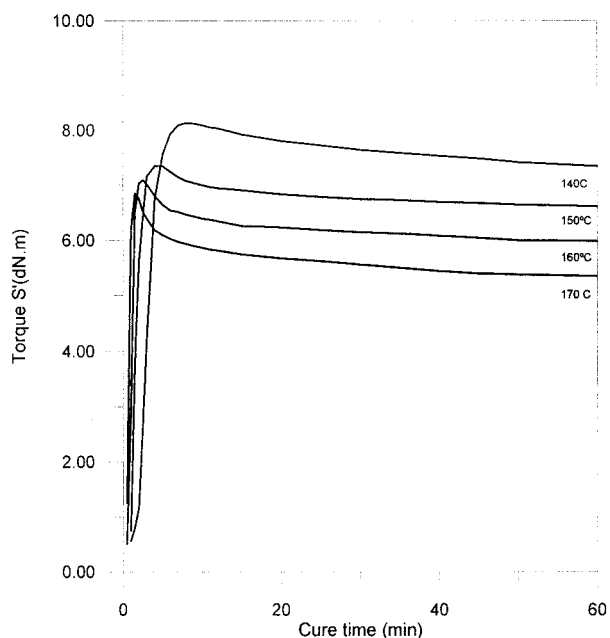

Figure 4 Rheometer curves at 150°C for compounds with different levels of DPTT and an equal content of TMTM.

should produce crosslinking in formulation 2 (TMTM only). This is not the case, and therefore implies that this mechanism would not take

Figure 3 Rheometer curves for compound 4/0 cured at different temperatures.

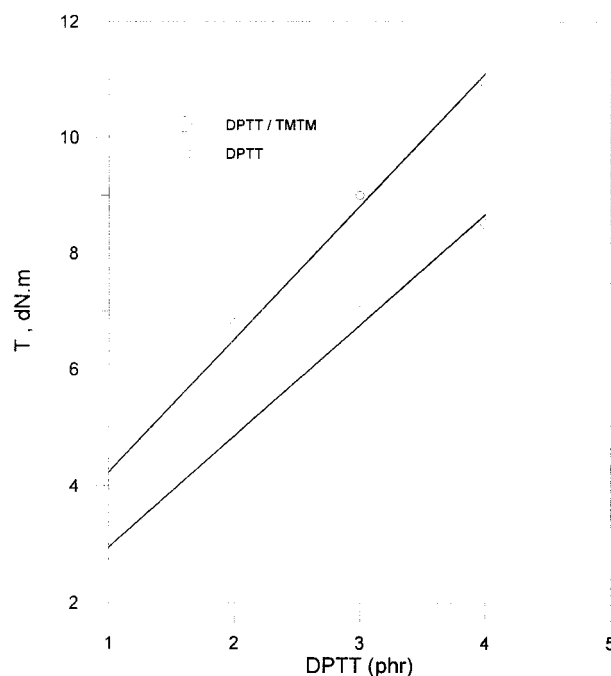**Figure 5** Changes in torque increment ($T_{max} - T_{min}$) for compounds with a different content of DPTT, alone and with equal content of TMTM.

**Table III   Rheometer Data for Compounds[a] Cured at 150°C**

Compound	1/0	1/1	2/0	2/1	2/2	3/0	3/1	3/2	3/3	3/4	3/6	3/8	4/0	4/4
t_{97}, min	3.2	11.6	2.9	5.8	9.5	2.9	3.7	6.1	8.2	11.1	20.7	35.6	3.0	8.1
T_{min}, dNm	0.5	0.4	0.4	0.2	0.3	0.3	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.3
T_{max}, dNm	2.3	4.2	4.8	5.8	7.1	6.3	6.9	7.8	9.1	9.5	9.5	9.2	7.5	10.9
Reversion,[b] %	17	2	11	2	2	11	3	2	3	3	0.7	0.1	10	3

[a] Compounds cured at 150°C.
[b] $(T_{max} - T_{60'})/(T_{max} - T_{min}) \times 100$.

place with TMTD either. The only way to explain crosslinking for these formulations would be to suggest disproportionation of the sulfurating agent with unreacted thiuram, and that only sulfurating agents with S>1 are able to produce crosslinking. (With TMTM alone, only S=1 species could be formed.) Or, this mechanism may not be correct, and other reactions could be taking place.

We arrive at the same qualitative result on the crosslinking if the monosulphenyl radical generated by thermal scission of TMTM or TMTD is unable to react with rubber. The monosulphenyl radical would preferentially participate in a sulphur exchange reaction with TMTD (a disproportionation), and the formed disulphenyl radical is the species with the capacity of producing a poly-

meric radical, that in turn can be saturated with a mono- or disulphenyl radical. This species is subsequently transformed into a crosslink, via allylic substitution or disproportionation.
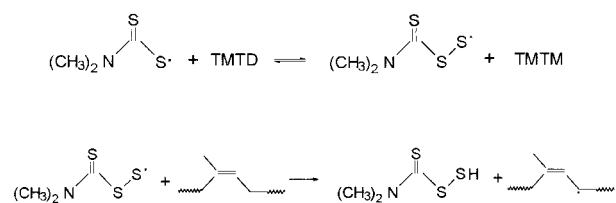
By this alternative route TMTM does not have the capacity to form a polymeric radical, whereas some crosslinking could occur by saturation between two polymeric radicals if the monosulphenyl radical can abstract an hydrogen from the polymeric chain.

Crosslink Reaction of NR with DPTT in the Presence of TMTM

Another sulphurating agent, DPTT, was used to widen the study of the vulcanization process of NR, as it holds more sulphur atoms in its structure than TMTD. ZnO and stearic acid were used as activators of the curing process.

Table II shows the formulations for natural rubber compound with DPTT, with the activators ZnO/stearic acid, and with or without TMTM. The crosslinking process was measured with an oscillating die rheometer. The rheograms of the compounds with DPTT alone cured at 150°C are shown in Figure 2. The curing reaction is essentially a first-order reaction, with very short induction times. The maximum torques are proportional to the DPTT concentration. The decrease in torque when vulcanization time increases can be attributed to a desulphuration reaction, with the
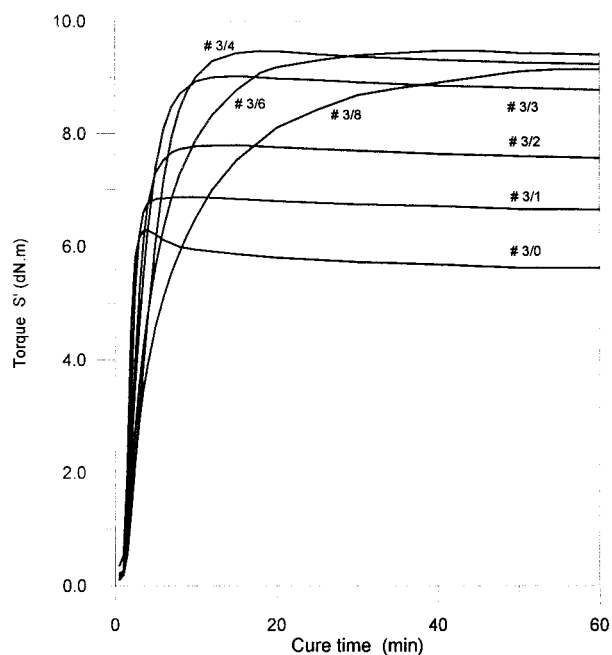

Figure 6   Rheograms for compounds with 3 parts of DPTT and a different content of TMTM.

polysulphydic structures breaking and the crosslink density decreasing with cure time. This phenomenon is favored with the increase of the cure temperature for compound 4/0 (Fig. 3). At 170°C, the relative concentration of —$S_{x>2}$— structures is greatly reduced when the compound is cured for 60 min.

Figure 4 shows the crosslinking progress at 150°C at different levels of DPTT with an equal content of TMTM, for compounds 1/1, 2/2, 3/3, and 4/4. In this case the desulphurating reaction almost does not take place, and a plateau is achieved at 60 min of vulcanization. The polysulphydic species, thermally unstable, must be practically absent on the cured network, and only di- and mono- sulphydic species, more stable, must constitute the crosslinks.

Compounds containing TMTM show a maximum torque far superior to the torque obtained with compounds containing only DPTT. Figure 5 displays the changes in torque increment ($T_{max} - T_{min}$) for compounds with different contents of DPTT, alone and with equal content of TMTM. The variation is linear with DPTT content, with TMTM present or not present, and both lines roughly parallel. The increase on ΔT can be explained if the sulphur atoms useful for crosslinking contained on the DPTT molecule do not participate with polysulphidic structures, only in di- and monosulphidic structures. For the same content of sulphur atoms more crosslinks are formed.

The cure data obtained for the compounds cured at 150°C are given in Table III. The minimum torque in the rheograph (T_{min}) can be taken as a measure of the viscosity of masticated rubber. The minimum viscosity values are found to be almost the same for all the compounds. Normally, the maximum torque (T_{max}) in the rheograph can be taken as the maximum viscosity of the rubber compound and is roughly a measure of the crosslink density in the sample. The optimum cure time (t_{97}) values increase with the addition of TMTM and this increase is higher for greater dosages of TMTM.

Figure 6 shows the rheograms for compounds with 3 parts of DPTT and different contents of TMTM, cured at 150°C. When TMTM is incorporated, reversion disappears and vulcanization rate is reduced, whereas the maximum torque increases up to 4 parts of TMTM. From this content, compounds reach similar torques.

Reversion, calculated from ΔT with cure time ($T_{max} - T_{60'}$), with respect to maximum ΔT (T_{max}

Table IV Physical Properties for the Compounds Cured

Compound	1/0	1/1	2/0	2/1	2/2	3/0	3/1	3/2	3/3	3/4	3/6	3/8	4/0	4/4
Cure time, t_{97}, min[a]	3.2	11.6	2.9	5.8	9.5	2.9	3.7	6.1	8.2	11.1	20.7	35.6	3.0	8.1
300% modulus, MPa[a]	0.6	1.0	1.2	2.2	2.0	1.7	2.1	1.9	3.0	1.8	3.0	—	2.4	—
Tensile strength, MPa[a]	6.0	12.5	14.5	24.5	24.5	34.0	27.4	21.2	21.6	20.5	17.7	2.3	24.4	2.0
Elong. at break, %[a]	800	800	740	690	680	750	670	590	520	480	500	290	640	200
Tensile strength, MPa[b]									12.8	1.7	2.3			
Elongation at break, %[b]									650	247	290			

[a] Compounds were cured at 150°C for their optimum cure time (t_{97}).
[b] Compounds were cured 60 min at 150°C.

Table V   Change in Crosslink Density, Poly-sulphidic, Di- and Mono-sulphidic Crosslinks[a]

Compound	1/0	1/1	2/0	2/1	2/2	3/0	3/1	3/2	3/3	3/4	3/6	3/8	4/0	4/4
Crosslink conc.,[b] mol/g 10^5	2.6	4.8	6.2	7.3	9.1	8.2	8.7	11.0	12.5	12.8	12.3	10.9	9.7	15.7
Crosslink conc.,[c] mol/g 10^5	—	—	5.3	—	9.0	6.2	—	—	12.2	12.6	12.1	11.3	—	—
Total S_x ($x > 2$) crosslink, %	70	52	—	65	32	28			—	—	—	—	62	26
Total S_2 crosslink, %	25	15	77	28	41	23			37	23	11	8	25	9
Total S_1 crosslink, %	5	33	23	7	27	49			63	77	89	92	13	65

[a] Compounds were cured at 150°C for their optimum cure time.
[b] Calculated with Flory–Rehner method.
[c] Calculated at 60 min of curing.

$-T_{min}$), is also registered in Table III. The presence of TMTM significantly reduces the reversion process, and therefore thermally unstable structures ($-S_{x>2}-$) are supposed to be almost absent in the final network.

Table IV gives the physical properties of the compounds cured at 150°C and their optimum times. Tensile strength of compounds without TMTM increases with DPTT content up to 3 parts and decreases for 4 parts, a normal behavior when crosslink density increases on the vulcanizates.

The tensile strength of 3/0 compound is very elevated and similar to the value obtained with the best vulcanized latex films. The physical differences between vulcanized latex and dry rubber arise from the absence of a mastication step. Tensile strength of 34 MPa has not been obtained before with dry unfilled rubber, only with vulcanizated latex films. Because the network obtained is very homogeneous, compound 3/0 has a high value of tensile strength. The different crosslink types ($-S_x-$, $-S_2-$ and $-S_1-$) are homogeneously distributed in the rubber matrix.

The presence of TMTM increases the tensile strength for series 1 and 2. However, for series 3 and 4, the effect is the reverse, and values drop as low as 2.3 MPa and 2.0 MPa for 3/8 and 4/4, respectively.

Table V shows the variation in the crosslink density for different compounds vulcanized at 150°C for their optimum times and for 60 min. Values were measured by equilibrium swelling in toluene and calculated with the Flory–Rehner method. Compounds containing only DPTT and cured for 60 min present a remarkable reduction in crosslink density. In compounds containing TMTM, crosslink density does not show variations with cure time. For compound 3/3, vulca-

nized for its optimum time (8.2 min), crosslink density is 12.5×10^{-5} mol/g, and when vulcanized for 60 min is 12.2×10^{-5} mol/g.

The relative content of the different crosslink types can be found in the bottom half of Table V. In compounds with only DPTT, polysulphidic crosslinks are predominant, but the trend is to be reduced when TMTM content is similar to DPTT content. In the compound series 3/0, from 3/3 compound polysulphidic crosslinks are not detected, and only di- and mono- sulphidic structures exist, increasing the latter with the increment on TMTM, and for compound 3/8, the network is virtually formed by only monosulphidic crosslinks.
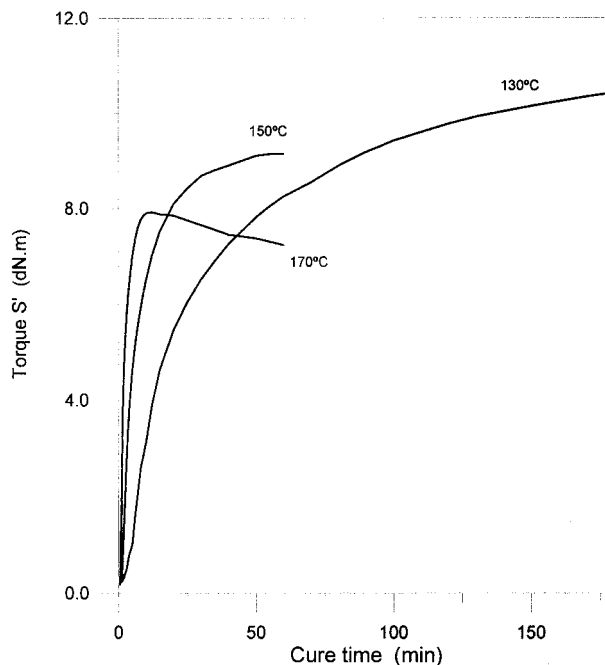
Figure 7 Rheograms for compound 4/4 at different vulcanization temperatures.

Crosslink densities for compounds 3/2 and 3/8 are identical (Table V), however, tensile strength values are dramatically different, 21.2 and 2.3 Mpa, respectively (Table IV). It is surprising that networks with a similar number of nodes present such different physical properties. Again, for compound 4/4 the crosslink density is 61% higher than for compound 4/0, whereas tensile strength values are 2.0 and 24.4 Mpa, respectively. These results show that TMTM presence in a vulcanization with a sulphur donor such as DPTT, not only produces networks with mainly monosulphidic links, but another reaction that favors the drop in physical properties must take place as well.

Figure 7 shows the rheograms for compound 4/4 at different vulcanization temperatures (130°, 150°, and 170°C). The reduction in torque with increasing temperature is evident, despite the fact that the network is almost exclusively formed by mono-sulphidic crosslinks, of high thermal stability. At 170°C, reversion is very important, and the vulcanized material extracted from the rheometer chamber is very stiff and brittle. The rheometer rotor crushes the rubber while it is in the chamber.

Compounds 3/6 and 3/8 were treated with methyl iodide in mild conditions in order to cleave monosulphidic crosslinks leaving intact disulphidic crosslinks. This treatment tests the existence of C—C crosslinks. These two compounds resulted in 12 and 20% of the total crosslink content, respectively. These C—C crosslinks could be formed by a homopolymerization reaction of the double bonds of close polymer chains, and could be initiated by persulphenyl radicals. This reac-
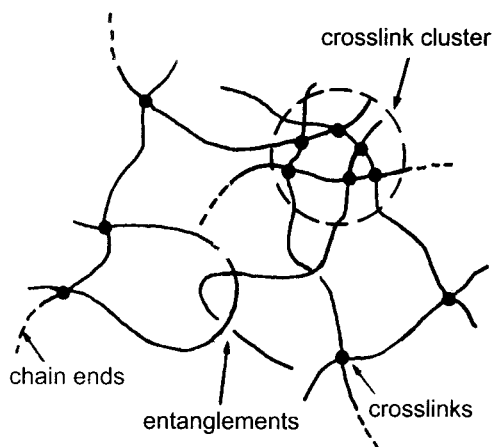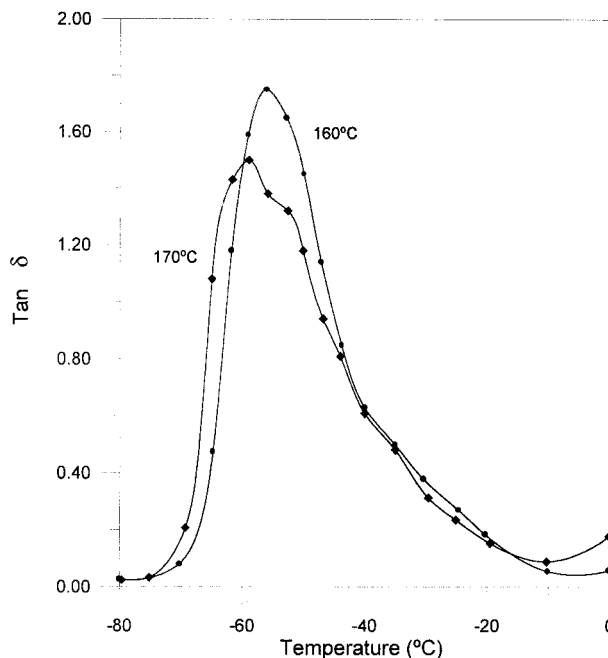

Figure 9 Loss tangent versus temperature for 3/6 cured at 160° and 170°C.

tion would be favored by temperature and TMTM concentration. This statement is not surprising as thiuram disulfides can act as initiators in some radical polymerizations.[16]

This possible additional reaction of the persulphenil radicals to double bonds may give rise to a polymerization between adjacent double bonds, and generate a small but densely crosslinked polymer volume, that at relatively small deformations acts as a rupture nucleus.[17] A network with such a texture will obviously possess lesser tensile strength than a uniform network. Figure 8 shows a schematic representation of a network structured in this way. This inhomogeneous crosslink distribution would adversely affect the physical properties.

Figure 9 shows the plot of the loss tangent for the sample 3/6 cured at 160° and 170°C respectively. The graph shows a wide absorption peak in the glass transition range of the polymer for the sample cured at 160°C, and for the sample cured at 170°C, a second relaxation in the higher temperature range, attributable to the lesser mobility of those polymer portions with the greatest crosslink density, that we considered to be clusters.[17]

Figure 8 Schematic of microstructural network features.

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