Cardanol Polysulfide as a Vulcanizing Agent for Natural Rubber

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Cardanol polysulfide (CPS), a sulfur donor type vulcanizing agent, was synthesized from a reaction of element sulfur and cardanol which separated from decarboxylated cashew nut shell liquid. The effect of CPS as a vulcanizing agent on the properties of rubber compounds was remarkable. The optimum cure time of rubber containing CPS was reduced and the mechanical properties were improved. Moreover, the CPS rubber was found to have lower reversion.

Key words: vulcanizing agent, cardanol and natural rubber.

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คาร์ดานอลพอลิซัลไฟด์สำหรับเป็นสารก่อวัลคะไนซ์ในยางธรรมชาติ

ลีลาวัลย์ ขาวขำ นฤมล สวัสดิ์พฤกษา นันทิตา คำทอง จำเรียง ธรรมธร และ
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คาร์ดานอลพอลิซัลไฟด์ (CPS) เป็นสารวัลคะไนซ์ประเภทที่ให้ซัลเฟอร์ สังเคราะห์ได้จากปฏิกิริยาของธาตุซัลเฟอร์กับคาร์ดานอลที่แยกได้จากดีคาร์บอกซิเลต ของเหลวจากเปลือกมะม่วงหิมพานต์ ผลของการใช้ CPS เป็นสารวัลคะไนซ์กับสารประกอบของยาง เป็นที่น่าประทับใจ ยางที่มี CPS ผสมอยู่จะใช้เวลาบ่มลดลงและสมบัติทางกายภาพดีขึ้น ยิ่งกว่านั้นพบว่ายางดังกล่าวมีค่ารีเวอร์ชันลดลงด้วย

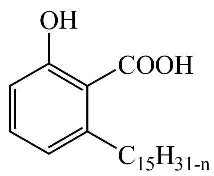
คำสำคัญ สารก่อวัลคะไนซ์ คาร์ดานอล ยางธรรมชาติ

INTRODUCTION

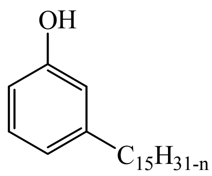
There are many ingredients in rubber compounds, and each ingredient has its specific function and impact on both properties and price. In order to reduce the cost of investment in compounds that are suitable for certain applications, knowledge of the function and effectiveness of compounding ingredients is indispensable.

Vulcanization is a chemical process by which the physical properties of natural or synthetic rubber are improved; finished rubber has higher tensile strength, increased resistance to swelling and abrasion and is elastic over a greater range of temperatures. In its simplest form, vulcanization is brought about by heating rubber with sulfur. One of the disadvantages of the process is reversion of the sulfur. The reversion increases with an increase in the amount of sulfur. Furthermore, it is easy for blooming to occur because sulfur has low solubility in rubber at room temperature. A sulfur donor is used to replace sulfur in order to solve this problem. Vulcanizing agents are substances which bring about the actual crosslinking process. The most important ones are sulfur, sulfur donors, selenium, tellurium, peroxides and metallic oxides.[1]

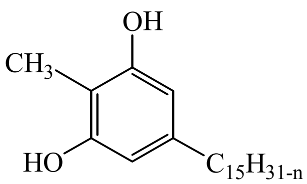
Cashew (*Anacardium occidentale*) is a member of the *Anacardiaceae* family. The cashew nut shell liquid (CNSL) is a by-product of the cashew industry. CNSL,[2] extracted with low boiling petroleum ether, contains about 90% anacardic acid and about 10% cardol. CNSL, on distillation, gives the pale yellow phenolic derivative cardanol. Natural CNSL contains 80.9% anacardic acid, 10-15% cardol and small amounts of other materials, notably the 2-methyl derivative of cardol. The chemical structures of major compounds in natural CNSL are shown in Figure 1. The side chains exist in saturated (n = 0), monoene (n = 2), diene (n = 4) and triene (n = 6) forms with cis configuration.[3-6]



anacardic acid
(6-pentadecenyl salicylic acid)

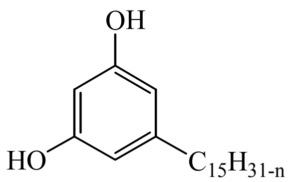


cardanol
(3-pentadecenyl phenol)



2-methyl cardol

(2-methyl, 5-pentadecenyl resorcinol)



cardol

(5-pentadecenyl resorcinol)

Where n = 0, 2, 4 or 6

Figure 1. Chemical structures of major compounds in natural CNSL.

In the roasting process, some polymerization as well as decarboxylation occurs because of the highly unsaturated nature of CNSL. Thus, a typical product would contain polymer (20-25%), cardanol (60-65%), cardol (10-12%) and other minor components.

CNSL, cashew nut shell liquid-formaldehyde resin(7) and phosphorylated derivative(8,9) have been used as vulcanizing agents for natural rubber. The results suggested that the presence of 10 ph of CNSL will decrease the state of cure time and increase the cure rate index and keep constant the rate of vulcanization. With the addition of cashew nut shell liquid-formaldehyde resin (5-15 ph), the physiomechanical properties of natural rubber lead to the improvement in processability of the mixes. Researchers claim this is because of plasticization of the mix.

This study involved synthesizing a vulcanizing agent from cardanol for use as a sulfur donor and studying the mechanical properties of the rubber which was prepared from the vulcanizing agent. The investigation is concerned with the preparation of cardanol polysulfide (CPS) from cardanol. The process was carried out under varying conditions such as reaction temperature and reaction time. CPS was used as a vulcanizing agent by mixing it with natural rubber and other additives. Finally, the vulcanization characteristics, mechanical properties and accelerated aging were determined.

MATERIALS AND METHODS

Chemicals

Cashew nut shell liquid (CNSL) was a gift from the 25 Industrial Products Co., Ltd. Natural rubber (grade STR20) was purchased from Thai Hua Co., Ltd. The chemicals for vulcanization such as N-cyclohexyl-benzothiazole-2-sulfenamide (CBS), naphthenic oil, stearic acid and carbon black were obtained from the Rubber Research Institute. Formaldehyde was purchased from Lab Scan. Resorcinol was purchased from Sigma. Elemental sulfur and zinc oxide were purchased from Fisher. Diethylenetriamine and petroleum ether was purchased from Fluka. Calcium hydroxide and deuterated chloroform were purchased from Merck. Ethyl acetate, hexane, methanol, toluene and propylene glycol were bought from local agents as commercial grade.

Preparation of CPS

Preparation of cardanol from CNSL(10-12)

All Infrared (IR) spectra were recorded using a Nicolet Impact 410 spectrometer. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Bruker ACF-200 spectrometer and the solvent used was $CDCl_3$. Sulfur content was determined using a LECO SC-132 sulfur analyzer. Non-productive compounds were mixed by a Kneader Machinery internal mixer. Vulcanization ingredients were added to the compounds on a Lab Tech Engineering two-roll mill. Cure characteristics at 150^{o}C for 30 min and arc 0.5^{o} were determined using a Monsanto rheometer MDR2000. Sheets and test specimens were vulcanized by Lab Tech Engineering TP-400 compression molding. Tensile measurements were carried out using an Instron Calibration Laboratory 1445 tensile tester. Hardness was determined using a Zwick hardness testing machine. Rebound resilience was determined using a Zwick rebound tester.

CNSL was decarboxylated to give cardanol in the presence of calcium hydroxide as a catalyst. Calcium hydroxide (4 g) with hexane (200 ml) as a solvent was charged into 200 g of natural CNSL in a 1000 ml 2-neck round bottom flask equipped with a condenser and a thermometer. The mixture was refluxed at a temperature of 120^{o}C and stirred for 3 h. The reaction was stopped and the mixture was cooled down. Calcium hydroxide was filtrated. After evaporation of the solvent, decarboxylated CNSL was obtained. IR and NMR spectra of the resulting product shown in Figures 3b, 4b and 5b indicate that the carboxylic acid group was removed completely.

Decarboxylated CNSL (60 g), formaldehyde (19.4 g) and diethylenetriamine (2.57 g) were mixed in methanol (200 ml). An exothermic reaction took place after mixing the reactants. After 30 minutes, two phases were formed. The upper phase was a slightly red solution. The lower phase was solidified and dark in color. The upper phase was decanted and treated with water (40 ml) followed by extraction with petroleum ether. The petroleum ether extract was distilled to recover hydrocarbon solvent. A reddish residue of cardanol (45 g, 80% w/w) was obtained.

Synthesis of CPS

Cardanol (70 g) and excess elemental sulfur (40 g) were added to a 250 ml beaker. Toluene or propylene glycol was used as a solvent at a reaction temperature of 110 or 185°C, respectively, according to the boiling point of each solvent. At other temperatures, no solvent was used. The mixture was heated to the desired temperature in a range of 110-185°C and stirred for 2 h. The reaction mixture became viscous resin. After stopping the reaction, the viscous resin was diluted with ethyl acetate with stirring for 0.5 h. The diluted mixture was allowed to stand for at least 3 h to let non-reacted elemental sulfur precipitate. Then, the mixture was filtrated and centrifuged to get rid of excess elemental sulfur. The diluted mixture was evaporated. Dry weight of the dilution was calculated. Sulfur content in CPS was determined using a sulfur analyzer. In order to determine the suitable reaction time to give the highest sulfur content in CPS, the reaction times were varied among 3, 4 and 5 h. To calculate the weight of CPS,[13] approximately 1.5 g of a sample was poured into a weighing bottle and the bottle was placed in a oven maintained at 135°C for 1 h. Then, it was taken out of the oven and was allowed to cool down in a desiccator. The mass was weighed and the content of nonvolatile resin was calculated to an integral number by the equation below.

$$N = D/S \times 100 \qquad \text{Equation 1}$$

Where, N is the content of nonvolatile matter (%), D the mass of sample after drying (g), and S the mass of sample (g).

Characterization of CPS

The product, cardanol polysulfide (CPS), is a dark brown resin. The characterization of cardanol and CPS was carried out by FT-IR, ^{1}H NMR and ^{13}C NMR. The chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Deuterated chloroform ($CDCl_3$) was used as a solvent for recording the NMR spectra. All spectra are presented in Figures 3c,d; 4c,d and 5c,d. Sulfur content in CPS was determined by a sulfur analyzer according to ASTM D 1552-00[14] using oxygen gas pressure of 400 psi, instrument gas pressure of 400 psi, and furnace temperature 1350°C.

Preparation of rubber compounds

a. Preparation of non-productive compounds

Non-productive compound is rubber containing additives in the absence of vulcanization ingredients. Rubber additives used in this research were resorcinol, naphthenic oil, carbon black, stearic acid and zinc oxide. The amount of each additive was the same as that in commercial non-productive compound, as shown in Table 1. The unit is the amount of an additive in grams per 100 grams of rubber or parts of the additive per 100 parts of rubber (phr).

The amounts of conventional rubber additives were used in typical amounts. The non-productive compounds were mixed by a banbury mixer using the following conditions; rotor speed of 43 rpm, mixing temperature of 110°C and mixing time of 6 min.

Table 1. Ingredients in non-productive compound.

Ingredients	Quantity of mix (phr)
Natural rubber (STR20)	100
Resorcinol	1.1
Naphthenic oil	3.5
Carbon black	24
Stearic acid	2
ZnO	3
	133.6

b. Preparation of productive compounds

Vulcanization ingredients were added to non-productive compounds and mixed by a two-roll mill using the following conditions, temperature of 70^{o}C, mastication time for non-productive compound of 2 min, and mixing time of 8 min.

CPS was used to partially replace sulfur by controlling the total sulfur at 2 phr. Normally, the amount of a sulfur donor, which was used to replace sulfur, is estimated from active sulfur. The CPS has 28 %wt of sulfur content but the amount of active sulfur cannot be determined. Thus 28 %wt of sulfur in CPS was used to calculate the required level of sulfur. The amount of CPS in the products in the compounds was varied at 1.79, 3.57, 5.36 and 7.14 phr.

Table 2 shows the vulcanization ingredients of rubber compounds used in this work. For studying the effect of CPS when using combinations of sulfur and sulfur donor for vulcanization, condition B, as shown in Table 3, was chosen to represent this system. The amounts of CPS were varied from 0 to 6 phr while sulfur content was kept constant at 1.5 phr (series B). For studying the effect of CPS when only a sulfur donor was present for vulcanization, condition E was chosen to represent this system. The amounts of CPS were varied from 0 to 15 phr without any sulfur in the productive compound (series E).

Table 2. Vulcanization ingredients of rubber compounds.

Compounds	**Vulcanization ingredients (phr)**		
	CBS	**Sulfur**	**CPS**
A	1.5	2.0	-
B	1.5	1.5	-
B1	1.5	1.5	1.79
B2	1.5	1.5	4.0
B3	1.5	1.5	6.0
C	1.5	1.0	-
C1	1.5	1.0	3.57
D	1.5	0.5	-
D1	1.5	0.5	5.36
E	1.5	-	7.14
E1	1.5	-	9.00
E2	1.5	-	12.0
E3	1.5	-	15.0

Determining vulcanization characteristics of the rubber compounds

Vulcanization characteristics and vulcanization curves were determined using a Monsanto rheometer MDR2000 according to ASTM D 2084-01.[(15)] The conditions of testing used are the following, temperature 150^{o}C, testing time 30 min and arc 0.5^{o}. The amount of CPS was varied to study the effect of CPS on vulcanizing the rubber compounds. Finally, the rubber compounds were determined and the vulcanization characteristics and the mechanical properties of rubber compounds were investigated.

Vulcanization procedures

The vulcanized rubber sheets were prepared by compression molding. The mold was preheated to avoid the long curing times at relatively low temperatures which are necessitated by the poor thermal conductivity of rubber. The mold was brought to curing temperature (150^{o}C) in the closed press and held at this temperature for at least 20 min before the green rubber pieces were inserted. After preheating the mold, green rubbers were inserted into the mold and the press was closed. The mold was held under a pressure of 120 kg cm^{-2} (1700 psi) on the cavity at 150^{o}C to the required vulcanization time for each piece. The vulcanized sheets were conditioned at 23 ± 2^{o}C for at least 16 h before preheating and testing.

Mechanical testing

The mechanical properties of the rubber compounds were determined using ASTM and ISO test methods as described in following sections. Hardness, tensile properties and rebound resilience were determined according to ASTM D 2240-02,[(16)] ISO 37:1994[(17)] and ASTM D 1054-91,[(18)] respectively. Accelerated aging was determined according to ASTM D 573-99 and ISO 188-1998.[19,20]

RESULTS AND DISCUSSIONS

CPS used as a sulfur donor type vulcanizing agent was prepared from the reaction of cardanol and elemental sulfur. Three parameters: reaction temperature, solvent and reaction time, were studied. CPS, including other common additives, was mixed with natural rubber sheet. The non-productive compound was prepared by using a banbury. The vulcanization ingredients comprising accelerator, sulfur and CPS were mixed with non-productive compounds by a two-roll mill.

Preparation of cardanol polysulfide (CPS)

Effect of reaction temperature and solvent on preparation of CPS

The effect of reaction temperatures from 110 to 185^{o}C on the sulfur content in prepared CPS was studied. Toluene or propylene glycol was used as a solvent with cardanol (70 g), elemental sulfur (40 g) and a reaction time of 2 h. Table 3 shows the effect of reaction temperature and solvent on the percentage of sulfur in CPS. The reaction at 140^{o}C in the absence of solvent was found to give the largest amount of sulfur in CPS. This shows that an increase in temperature results in an increase in the number of free radicals leading to an increase in the rate of polymerization. When a reaction temperature of 160^{o}C was used, the sample could not be studied because the mixture was too viscous to stir.

Effect of reaction time on preparation of CPS

It can be seen from Figure 2 that when the reaction time increases from 2 to 3 h, the sulfur content in CPS increases from 24%wt to 28%wt. Insignificant differences of sulfur content in CPS is found for the reaction time in a range of 3 to 5 h. This indicates that the completed reaction occurs within 3 h. Thereof, the reaction time of 3 h and a temperature of 140^{o}C were chosen for further experimentation. Figure 2 shows the amount of sulfur in CPS as a function of reaction time, using a reaction temperature of 140^{o}C.

Previous work[(13)] reported that the vulcanizing agent from CNSL has 30%wt of sulfur. For this research, the vulcanizing agent from cardanol had 28%wt of sulfur. The comparison indicated an insignificant difference of %wt of sulfur. Consequently, cardanol can react with elemental sulfur as well as CNSL under the same conditions.

Table 3. Effect of reaction temperature and solvent on the %wt of sulfur content in CPS: reaction time = 2 hrs.

Temp. (°C)	Solvent	%wt of sulfur content	Remarks
110	Toluene	10	-
120	no solvent	17	-
140	no solvent	24	-
160	no solvent	-	The reaction cannot reach 2 hrs because the mixture was too viscous to stir.
185	Propylene glycol	10	-

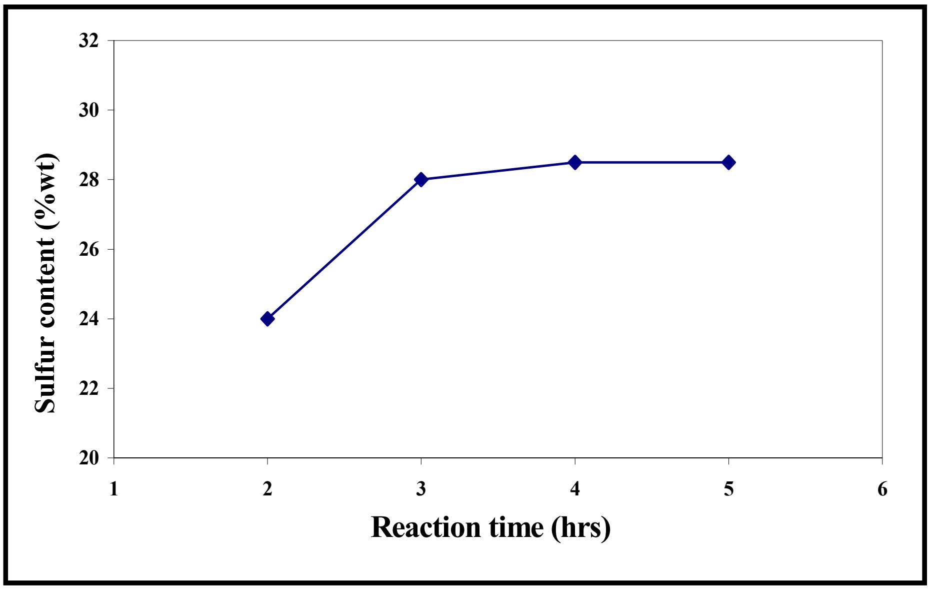


Figure 2. Effect of reaction time on the amount of sulfur content in CPS: cardanol 70 g, elemental sulfurs 40 g and reaction temperature 140°C.

Characterization of CPS

Figures 3, 4 and 5 show FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra of cardanol and CPS. The difference between Figures 4c and 4d (^{1}H-NMR spectra of cardanol and CPS, respectively), indicates that there are less double bonds in the alkyl chain in CPS than in cardanol. ^{1}H-NMR illustrated that olefinic protons (4.85-5.95 ppm) of CPS mostly disappear.

Thus, CPS obtained from the reaction of cardanol and S_8 may have sulfur addition of some double bonds of a side chain of cardanol. The reaction and possible structure of CPS are proposed.

S_X may be a linear linkage of the sulfur atom, such as –S-, -S-S-, -S-S-S-, etc. Also, it is believed that CPS is a complex mixture of sulfide resin, comprising mono-, di- and polysulfide linkage.[21-23]

Normally, vulcanizing agents influence such vulcanization characteristics as optimum cure time (t_{90}), delta torque, etc. Moreover, CPS may be used as a sulfur donor in place of sulfur (S_8) with the same required level of sulfur (2 %wt) in the vulcanization process. The amount of sulfur donor, which may be compounded with the rubber, is sufficient to provide an equivalent amount of sulfur as if sulfur itself was used. The effect of CPS in rubber compounds on the vulcanization characteristics was studied using a Monsanto rheometer MDR2000 according to ASTM D 2084-01[15] at a vulcanizing temperature of 150°C for 30 min and arc 0.5°. The data of vulcanization characteristics are shown in Table 4.

Vulcanization characteristics of rubber compounds A-E (using CPS in place of sulfur by controlling total sulfur at 2 phr)

The effects of CPS on the vulcanization characteristics and the vulcanization curve when using CPS in place of sulfur were determined by rheometry. The results were compared for rubbers containing CPS with total sulfur of 2 phr (compounds B1, C1, D1 and E) and rubbers without CPS (compounds A, B, C and D).

Extent of crosslinking

The delta torque or the extent of crosslinking is represented as the degree of crosslinking. The delta torque of rubbers containing CPS are more elevated than that of rubbers without CPS. This indicates that CPS can liberate sulfur to crosslink with the molecules of rubber, hence the degree of crosslinking was found to increase. Moreover, in series B which contained sulfur, it can be seen that the extent of crosslinking slightly increases with an increase in the amount of CPS. It can be seen that the extent of crosslinking of rubber compounds in series E increases with the amount of CPS increase. The reason for the change in the extent of crosslinking due to CPS is as previously mentioned.

Optimum cure time (t_{90})

The effects of CPS and elemental sulfur on the optimum cure time and vulcanization curves of rubber were compared. The results are shown in Table 4; compound E (rubber containing only CPS) has the longest optimum cure time. On the other hand, compound A (rubber containing only sulfur) was found to give a shorter optimum cure time. This is because a large amount of CPS resulted in a low rate of vulcanization leading to the long optimum cure time. Since, as previously observed, one vulcanization process effected by CPS is an increase in crosslinking, it can be explained that for compounds B, B1, B2 and B3 when the amount of CPS increased, the time to onset of vulcanization decreased. As the rate of vulcanization becomes faster, shorter optimum cure time results. The optimum cure time of rubber compounds in series E decreased as the amount of CPS was raised. It can be observed that this result is quite similar to those of series B. This indicates that when there is no effect from sulfur, CPS can reduce the cure time because it reduces the onset of vulcanization to an earlier state. It is confirmed, that under the appropriate conditions, the cure time can be reduced by CPS.

Mechanical properties of rubber compounds

Mechanical properties, such as tensile properties, hardness and rebound resilience, of the rubber compounds were investigated using the three variables tested CPS systems, *i.e.* using CPS in place of sulfur, using CPS combined with sulfur and using only CPS for vulcanization. Table 5 shows the values of tensile strength, elongation, modulus 500%, hardness and rebound resilience.

Mechanical properties of compounds A-E (using CPS in place of sulfur by controlling total sulfur at 2 phr)

The effect of CPS on the mechanical properties of rubbers when total sulfur was controlled at 2 phr and rubbers without CPS (compounds A-E) were studied. The results were compared between rubbers containing CPS (compounds B1, C1, D1 and E) and rubbers without CPS (compounds A, B, C and D).

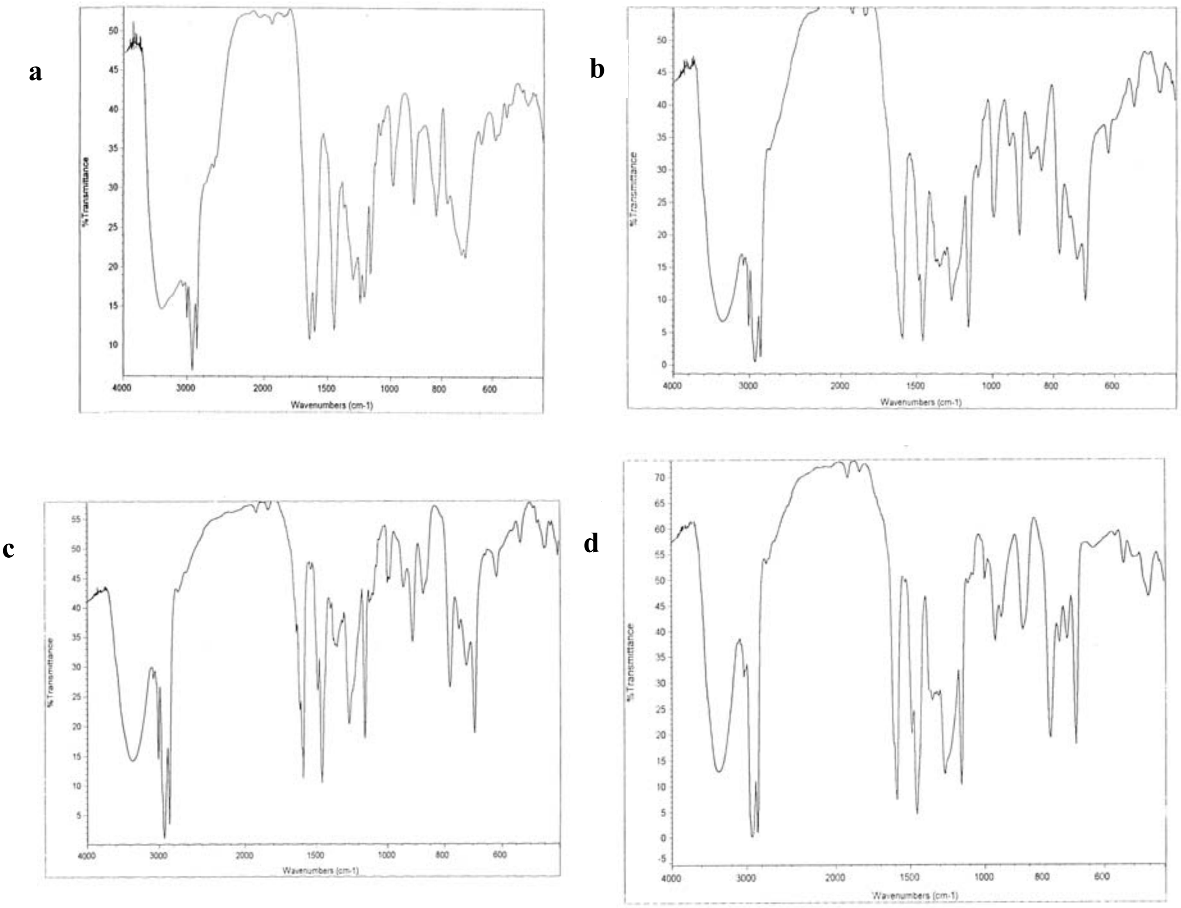


Figure 3. IR spectra of a) CNSL b) decarboxylated CNSL c) cardanol and d) CPS.

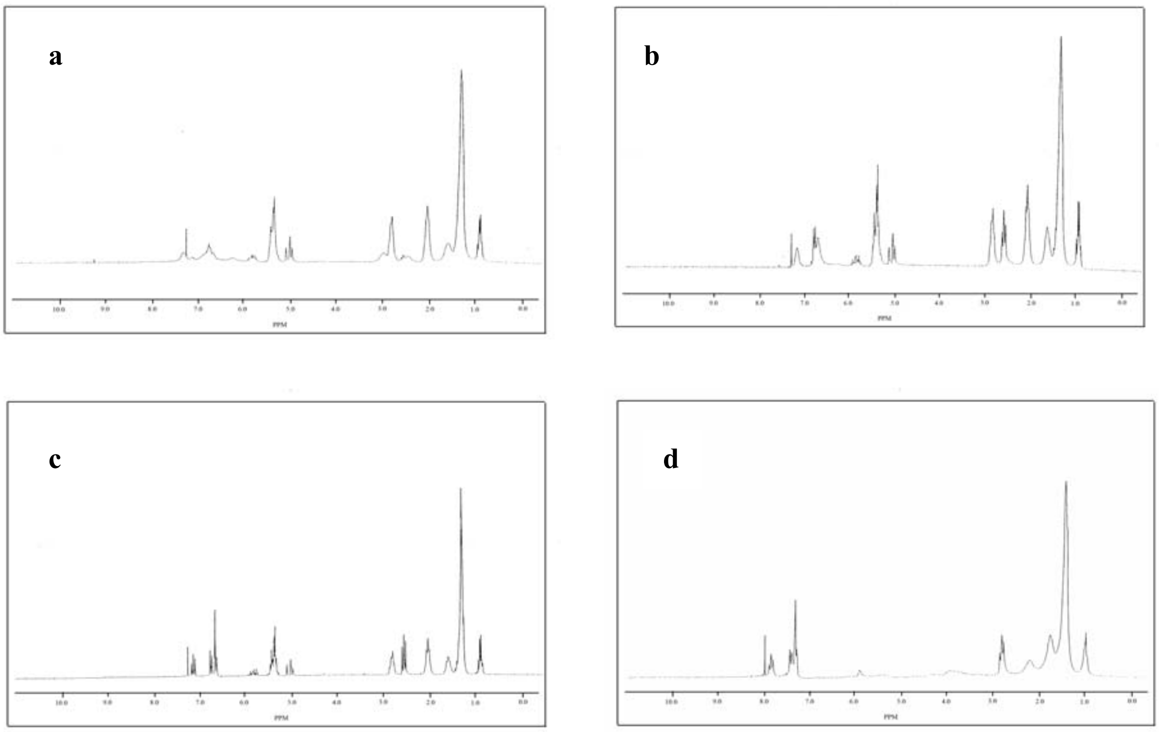


Figure 4. ^{1}H-NMR spectra of a) CNSL b) decarboxylated CNSL c) cardanol and d) CPS.

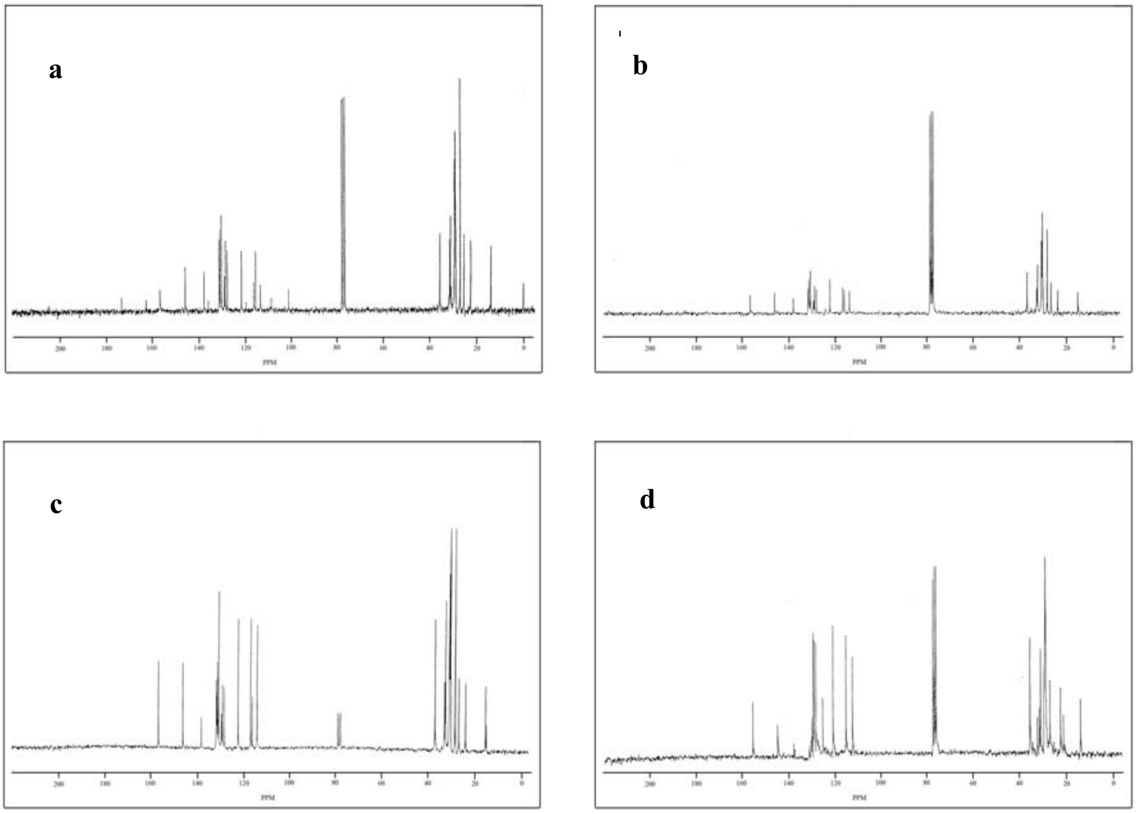


Figure 5. ^{13}**C-NMR spectra of a) CNSL b) decarboxylated CNSL c) cardanol and d) CPS.**

Table 4. Vulcanization characteristics of rubber compounds.

Compounds	Min τ	Max τ	Delta τ	T_{90}	Rate (phr)
A	1.21	9.50	8.30	5.65	0.68
B	1.14	8.87	7.74	5.71	0.58
B1	1.16	9.44	8.29	5.43	0.46
B2	1.11	9.61	8.50	5.26	0.42
B3	1.08	10.32	9.24	5.19	0.41
C	1.22	8.82	7.60	6.20	0.53
C1	1.12	9.16	8.05	6.07	0.51
D	1.21	6.79	5.58	6.27	0.51
D1	1.05	8.81	7.76	6.32	0.46
E	0.93	8.40	7.47	6.40	0.37
E1	0.89	8.72	7.83	5.82	0.51
E2	0.88	8.78	7.90	5.57	0.50
E3	0.89	8.91	8.02	5.18	0.61

Table 5. Effect of CPS content on the mechanical properties of rubber compounds.

Compounds	Tensile strength (MPa)	Elongation at break (%)	Modulus 500% (MPa)	Hardness (Shore-A)	Rebound resilience (W/mm)
A	24.2	613	16	46.40	79.8
B	24.1	619	14	44.80	76.8
B1	26.0	633	14	46.45	80.1
B2	24.8	644	14	46.85	82.7
B3	24.0	679	13	48.90	83.1
C	23.6	635	14	43.05	74.4
C1	24.7	645	12	45.75	79.1
D	21.9	643	13	37.00	69.8
D1	23.7	657	12	44.55	78.7
E	14.8	665	10	43.70	69.5
E1	15.3	672	10	45.25	70.4
E2	16.4	677	11	45.90	76.5
E3	17.5	688	12	46.65	78.0

Tensile properties

The effect of CPS on the tensile properties of rubber compounds were compared between rubbers containing CPS (compounds B1, C1, D1 and E) and rubbers without CPS (compounds A, B, C and D). The results are shown in Table 5. The tensile strength of rubbers containing CPS are higher than those of rubbers without CPS. The tensile strength increases because the degree of crosslinking increases from the sulfur which was liberated from CPS. Elongation of rubbers containing CPS is higher than that of rubbers without CPS. This is because atoms of CPS containing cardanol can crosslink with the molecules of rubber leading to high mobility of the molecular chains and resulting in high elongation.

The modulus 500% had the same trend. The reason for these observed effects of rubbers containing CPS is that the CPS consists of cardanol that can crosslink with the molecules of rubber leading to high mobility of the molecular chains.

Hardness (Shore-A)

The hardness of the rubber compounds is shown in Table 5. It can be seen that the hardness of rubbers containing CPS is higher than that of rubbers without CPS. This indicated that CPS could be used as a vulcanizing agent to crosslink with the molecules of rubber, and also to increase the degree of crosslinking. As the degree of crosslinking increases, the hardness progressively increases.

Rebound resilience

The effect of CPS components on rebound resilience of rubber compounds is presented in Table 5. Analysis of rebound resilience revealed that incorporation of large amounts of CPS resulted in the improvement of rebound resilience, but it decreased when the amount of CPS increased beyond an optimal amount. The trend of rebound resilience is not dependent on the degree of crosslinking. Based on the degree of crosslinking, rubber elasticity is affected by the crosslink structure. Elasticity increases with increased crosslinking, thus raising the rebound resilience to an optimum value.(24) As the number of crosslinks increases, the molecules or their segments become so firmly attached to one another that their tendency to return to the basic position after deformation ceases.

Mechanical properties of series B

The effect of CPS content in rubber compounds on the mechanical properties was investigated when the amount of sulfur was kept constant at 1.5 ph.

Tensile properties

The effect of CPS content on the tensile properties of rubber compounds for series B is shown in Table 5. The rubber containing CPS of 2 ph has a tensile strength higher than the rubber without CPS. Addition of CPS greater than 2 ph into the rubber resulted in a decrease in the tensile strength of the rubber. Tensile strength rises with the number of crosslinks until an optimum is reached after which, if the crosslinking is continued (in which case over-crosslinking takes place), it initially falls steeply.(25)

Hardness (Shore-A)

Table 5 shows the hardness of rubber compounds of series B. The hardness of the rubber compounds improved when the CPS content increased. This is due to the fact that the high degree of crosslinks in the rubber give high values of hardness to the rubber.

Moreover, the elongation of the rubber was improved by increasing the amount of CPS. This, as previously mentioned, is because as the proportion of CPS increases, the network obtained from cardanol results in high mobility of molecular chains. The definite modulus or definite degree of crosslinking is related to the length of the crosslinking. The modulus of rubber decreased when increasing CPS in the rubber. This is because CPS liberates sulfide and crosslinks with the molecules of rubber. The network structures of CPS are obtained from cardanol that has a long chain of alkyl phenol. Thus it may be expected that the network structures consist of long bridge links having free mobility of chain segments leading to low modulus. On the other hand, if the network is obtained from only sulfur atom, the distance between the chains is not so long, thus the modulus is high. The longer the chain is the lower the modulus value.

Rebound resilience

The effect of CPS content on rebound resilience in rubber compounds for series B is detailed in Table 5. The rebound resilience of rubber compounds was improved when the CPS content increased. The result shows that the degree of crosslinking increased with CPS, thus the rebound resilience improved due to higher degree of crosslinking.

Mechanical properties of rubber compounds in series E

The effects of CPS content in rubber compounds for series E on mechanical properties were observed.

Tensile properties

The effects of CPS content on tensile properties of rubber compounds in series E are shown in Table 5. The tensile strength of the rubber was increased when the CPS content increased. This is due to an increase in the degree of crosslinking of the rubber. The elongation of the rubber compounds increased when the amount of CPS increased for the same reason as mentioned earlier. The modulus of the rubber compounds for series E was increased. This is because the rubber compounds in series E are the rubbers containing only CPS, hence, the distance of chain segments of each compound are short. Thus, the modulus was independent of the degree of crosslinking.

Hardness (Shore-A)

The hardness of rubber compounds in series E was improved when the CPS content increased. This indicated that the hardness is increased when the degree of crosslinking is increased.

Rebound resilience

The rebound resilience of rubber compounds in series E was improved when the CPS content increased. This indicates that the increase in rebound resilience was based upon the degree of crosslink. The result of this experiment is quite similar to the rebound resilience of series B rubbers containing various concentrations of CPS and elemental sulfur of 1.5 ph which shows an increasing rebound resilience of series B.

Effect of CPS on the accelerated aging test of rubber compounds

The difference in ultimate elongation before and after heating is the most useful criterion for judging the durability of vulcanized rubbers. The ultimate elongation of practically all vulcanized rubbers decreases during aging; the rate of decrease depends on temperature, time, and composition of yellow rubbers. In this research, the specimens were placed in an oven at 100°C for 1 or 3 days, then the mechanical properties of the aged specimens were investigated. The results are shown in Appendix G. The percentage changes in mechanical properties *i.e.*, tensile strength, elongation, modulus 500% and hardness or % reversion (compared to unaged specimens) were calculated and shown in Table 6.

Effect of CPS on the accelerated aging test of compounds A-E

The effect of CPS on the accelerated aging of compounds A-E was studied. The results of rubbers containing CPS were compared to rubbers without CPS.

Reversion of tensile properties

From Table 6 it can be seen that all reversion of the tensile properties, i.e. tensile strength, elongation at break and modulus 500%, show that rubbers containing CPS have lower reversion than rubbers without CPS. This can be explained in that CPS may have mono-, di- or polysulfide linkages which are stronger bonds than polysulfide from elemental sulfur. Besides, CPS may crosslink with the molecules of rubber by carbon-carbon bonds from unsaturated alkyl chains of cardanol. When the bond energy is high, the compounds will have good heat stability (see Table 7). This indicates that CPS has anti-reversion properties.

Reversion of hardness

The values for modulus and hardness of the rubber compounds were subjected to accelerated aging (or prolonged storage at room temperature) testing. It can be explained that the post-vulcanization which takes place from the accelerated aging test (or prolonged storage at room temperature) is due not only to the incorporation of additional free sulfur after the vulcanization, but also to some extent [(1)] to the shortening of the polythioether bridges and the simultaneous formation of additional crosslinks. In this reaction, an S_x bridge is, of course, split before being re-established after its shortening. In this splitting of the sulfur chains, which are incorporated as bridge links, the renewed crosslinking also takes place. Accelerators, which are able to activate free sulfur, are also capable, as far as they survive the vulcanization process without being decomposed, of activating and splitting crosslinked polythio chains, leading to the increasing hardness after accelerated aging. Moreover, % reversion of the hardness of rubbers containing CPS is higher than rubbers without CPS. This confirms the anti-reversion properties of CPS.

EFFECT OF CPS CONTENT ON THE ACCELERATED AGING TEST OF RUBBER

Effect of CPS content on accelerated aging test of rubber compounds containing elemental sulfur of 1.5 ph (series B)

The effects of CPS on accelerated aging test of rubber compound of series B were investigated.

Reversion of tensile properties

From Table 6, it can be seen that % reversion of tensile strength and elongation of rubber compound of series B decreases with an increase in CPS. Moreover, at 0 and 1.79 ph of CPS in rubber, the modulus values could not be measured, therefore % reversions were not obtained. The results show the improvement of hardness after aging even as the degree of crosslinking increases. This indicates that CPS can reduce the reversion of rubber compounds.

Table 6. % Reversion of rubber compounds.

% reversion	Tensile Strength (MPa)		Elongation at break (%)		Modulus 500% (MPa)		Hardness (Shore-A)	
	1 day	3 days	1 day	3 days	1 day	3 days	1 day	3 days
A	-34.98	-62.99	-30.32	-56.47	N.D.	N.D.	2.30	2.50
B	-29.41	-56.62	-23.87	-51.50	N.D.	N.D.	1.25	2.30
B1	-22.34	-46.11	-23.37	-50.78	N.D.	N.D.	1.30	2.50
B2	-14.45	-36.96	-19.51	-41.00	15.02	N.D.	1.90	3.00
B3	-11.07	-34.57	-19.02	-40.33	16.41	N.D.	2.40	3.00
C	-28.61	-40.41	-16.70	-45.03	10.79	N.D.	1.45	2.00
C1	-18.87	-28.63	-15.79	-34.57	15.39	N.D.	2.20	2.30
D	-20.95	-31.62	-14.68	-41.42	14.10	N.D.	1.35	2.10
D1	-20.22	-26.04	-14.66	-22.50	16.24	19.85	2.55	2.60
E	-19.82	-24.39	-13.77	-17.61	18.12	21.66	2.55	2.75
E1	-15.55	-18.13	-12.77	-16.61	18.53	23.59	2.60	2.80
E2	-11.98	-17.02	-10.74	-16.64	19.13	27.67	2.50	2.80
E3	-8.64	-17.54	-9.38	-15.95	19.75	28.73	3.00	3.20

<u>Note</u>

N.D.= cannot determine

Table 7. Bond energy of various types of crosslink[1].

Types of linkage	Bond energy (kcal/mol)
-C-S_x-C-	< 64
-C-S-S-C-	64
-C-S-C-	68
-C-C-	84

Effect of CPS content on the accelerated aging test of rubber compounds without sulfur (series E)

The effects of CPS on the accelerated aging test of rubber compounds in series E were observed.

Reversion of tensile properties

From Table 5, it can be seen that rubber compounds in series E have a low % reversion for most of the mechanical properties. The reason for this is that the sulfur linkage is spitted and re-established again after aging. This also indicates that CPS can reduce the reversion.

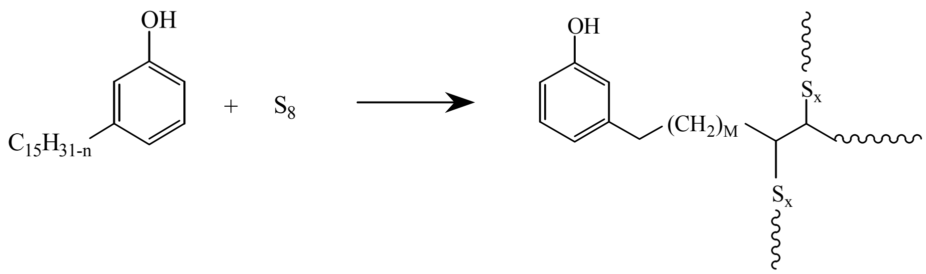


Figure 6. Schematic of proposed chemical structure of CPS.

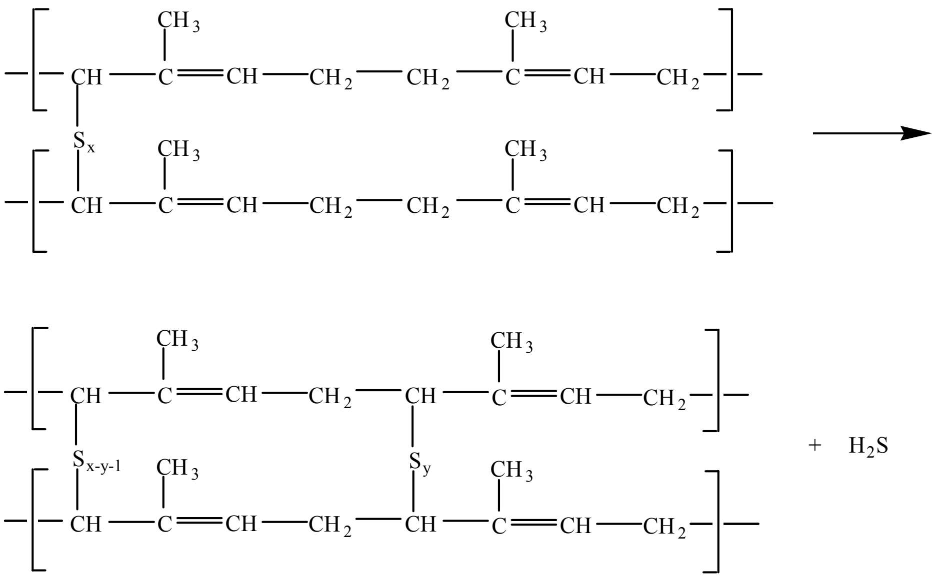


Figure 7. Splitting of sulfur bond after vulcanization Adapted from *Vulcanization* and *Vulcanizing Agents*.[1]

CONCLUSIONS

In this work, 80% wt/wt cardanol was separated from decarboxylated CNSL and used for preparation of cardanol polysulfide (CPS) as a vulcanizing agent. The appropriate conditions for the preparation of CPS were a reaction temperature of 140°C, non-solvent, a reaction time of 3 h and excess elemental sulfur, giving 28 %wt of sulfur content. From FT-IR, ^{1}H NMR, ^{13}C NMR and a sulfur analysis, CPS is a complex mixture of sulfide resin, comprising mono-, di-, polysulfide linkages between double bond carbons of an alkyl side chain of cardanol.

CPS, used as a vulcanizing agent, is mixed with natural rubber and other additives. The vulcanization characteristics and mechanical properties of vulcanized rubbers were tested. The vulcanization characteristics are delta torque and optimum cure time, and the mechanical properties are tensile strength, elongation, modulus, hardness and rebound resilience. The optimum cure time of rubber containing CPS was reduced and delta torque was increased when the CPS content was increased. Rubber containing CPS was found to have mechanical properties better than rubber without CPS. Then accelerated aging test was investigated and the results were compared to un-aged specimens. It was found that the CPS containing rubbers have lower reversion in the vulcanizates. This work showed that CPS can be used as a vulcanizing agent, improves the mechanical properties of the rubber and reduces the reversion of rubber.

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