

New Methods of Crosslinking Natural Rubber. Part I. The Introduction of Carboxylic Acid and Ester Groups into Natural Rubber and Their Subsequent Utilization for Crosslinking

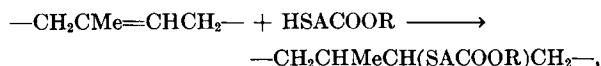
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INTRODUCTION

The aim of this work has been to introduce carboxylic acid groups into natural rubber (NR) so that the modified NR could be crosslinked by metallic bases, in a similar manner to the crosslinking of synthetic rubbers containing carboxylic acid and ester groups by salt formation to give vulcanizates which have unusual stress-strain properties.¹⁻³ For example, their tensile strengths were high in the absence of reinforcing fillers, in contrast to the very weak products obtained with conventional sulfur vulcanization systems.

Introduction of the carboxyl groups into NR was effected by treatment with a bifunctional reagent containing a thiol group and a carboxylic acid or ester group (cf. ref. 4), the principle being that the thiol group adds to the polyisoprene double bonds thus:



leaving the other functional group available for subsequent crosslinking reactions. Several bifunctional reagents of this type (where A is alkylene or arylene, and R is H, alkyl, or aryl) have been investigated but most of the work was carried out with ethyl thioglycollate, (A and R are CH₂ and C₂H₅, respectively).

EXPERIMENTAL METHODS AND MATERIALS

Materials

For the reactions in solution or in the dry state, the NR was pale crepe, either unmilled or milled on a two-roll mill in order to reduce its molecular weight (Found: $[\eta]$ 3.6 (g./100 ml.)⁻¹; Mooney viscosity 51, measured at 100°C. by the method of British Standard 1673: Part 3: 1951). The pale crepe was extracted by hot acetone for 24

hours under nitrogen. For reactions in latex, a recentrifuged, ammonia-preserved concentrate containing about 60% by weight of NR was normally used, preliminary experiments having shown that use of ordinary, once-centrifuged, NR latex leads to inconsistent results.

Thiol Compounds

Thioglycollic acid, its ethyl, *n*-butyl, and *n*-octyl esters, and the ethyl ester of 3-mercaptopropionic acid were commercial samples which were purified by distillation before use. The 4-mercaptoputanoic and 6-mercaptophexanoic acids were prepared by treatment of the corresponding bromocarboxylic acids with potassium ethyl xanthate,⁵ and *p*-mercaptopbenzoic acid was prepared from *p*-toluenesulfonic acid.⁶ Treatment of 2-bromooctanoic acid with potassium thiocyanate and aniline and subsequently with ammonia gave the anilide of 2-mercaptopoctanoic acid, which on hydrolysis with concentrated hydrochloric acid gave 2-mercaptopoctanoic acid. Heating a mixture of undec-10-enoic acid and thiolbenzoic acid at 60° for 3 hours gave 11-benzoylthioundecanoic acid, which was purified by crystallization from light petroleum (b.p. 40-60°); hydrolysis of this with potassium hydroxide gave 11-mercaptopundecanoic acid, for which a wide range of melting points have been previously reported.⁷ Reduction of di-4-carboxymethylphenyl disulfide⁸ with zinc dust and boiling acetic acid gave 4-mercaptopphenylacetic acid, which was purified by crystallization from a mixture of equal volumes of carbon tetrachloride and light petroleum (b.p. 40-60°).

The esters of the above acids were obtained by esterification with the appropriate alcohol and dry hydrochloric acid in the usual way. The physical characteristics of the new thiol compounds are given in Table I.

TABLE I
 Physical Characteristics of Thiol Compounds

	b.p., °C./mm. Hg	m.p., °C.	n_D^{25}	C, %		H, %		S, %	
				Found	Calc.	Found	Calc.	Found	Calc.
SH(CH ₂) ₅ COOEt	121/17	—	1.4611	54.9	54.5	9.3	9.2	17.9	18.2
C ₆ H ₅ COS(CH ₂) ₁₀ COOH	—	63–65	—	66.9	67.1	7.9	8.1	10.2	10.0
HS(CH ₂) ₁₀ COOH	—	48–49	—	60.6	60.5	10.2	10.2	14.5	14.7
HS(CH ₂) ₁₀ COOEt	124/0.03	—	1.4653	63.2	63.4	10.6	10.6	12.8	13.0
Me(CH ₂) ₅ CH(SH)COOH	108/0.04	—	1.4740	54.4	54.5	9.2	9.2	17.9	18.2
Me(CH ₂) ₅ CH(SH)COOMe	—	—	1.4590	57.0	56.8	9.7	9.5	16.7	16.8
HSC ₆ H ₄ CH ₂ COOH	—	105	—	57.1	57.2	4.8	4.8	18.9	19.1
HSC ₆ H ₄ CH ₂ COOMe	102/0.01	—	1.5650	59.3	59.3	5.7	5.5	17.5	17.6

Other Materials

Hydrogen peroxide (100 vol.), ascaridole, cumene hydroperoxide (75% by weight pure hydroperoxide), *p*-menthane hydroperoxide (52% by weight pure hydroperoxide), α, α' -azoisobutyronitrile (AIBN), and the stabilizer Ethomeen 18/60 (a condensate of stearylamine with ca. 50 ethylene oxide molecules) were commercial specimens.

Methods

Reactions with Dry NR and NR in Solution

The thiol compound, catalyst, and benzene (if required) were added to the rubber and the mixture was sealed *in vacuo*, allowed to stand for 3 days at room temperature, and then heated for 24 hours at 75°. The product was extracted with hot acetone under nitrogen for 24 hours, dried *in vacuo*, and analyzed for combined sulfur.

Reactions in NR Latex

These were carried out in a manner very similar to those previously described by Cunneen and Shipley.⁹ An aqueous solution of a stabilizing soap, usually an amine-ethylene oxide type of compound such as Ethomeen 18/60 was first added to the latex which was acidified with hydrochloric acid to pH 1. The catalyst and thiol compound were then added, and the reaction carried out under various specified conditions of time, temperature, pH, and amount of solvent. Coagulation was effected by pouring the latex into ethanol or acetone, and the wet coagulum so obtained was thoroughly extracted with hot acetone under nitrogen and dried before analyses and technological evaluations were carried out.

Reaction of Ethyl Thioglycollate with 1-Methylcyclohexene

To an emulsion of the olefin (19 g.), 0.05*N* HCl (100 ml.), and stabilizer (1 g.), was added

ethyl thioglycollate (12 g.) and *p*-menthane hydroperoxide (1 g.), and the resulting emulsion kept for six hours at room temperature. Working up in the usual way gave 9 g. of the ethyl ester of 2-methylcyclohexylthioglycollic acid (b.p. 83°/0.1 mm., n_D^{18} 1.4902).

ANAL.: Calc. for C₁₁H₂₀O₂S: C 61.2%, H 9.3%, S 14.8%. Found: C 61.0%, H 9.2%, S 15.1%.

The ester was dissolved in ethanol and hydrolyzed by refluxing for 30 minutes with 20% aqueous potassium hydroxide. The identity of the 2-methylcyclohexylthioglycollic acid so obtained was established by oxidation by the standard procedure¹⁰ to the corresponding sulfone¹⁰ (m.p. 96°).

ANAL.: Calc. for C₉H₁₆O₄S: C 49.1%, H 7.3%, S 14.6%. Found: C 48.9%, H 7.2%, S 14.5%.

Hydrolysis of NR-Ethyl Thioglycollates

A typical hydrolysis was carried out as follows. NR latex was treated with ethyl thioglycollate in the presence of *p*-menthane hydroperoxide in the usual way. To the modified latex (390 ml. containing 132 g. of rubber and 9.7% combined ester) was added 6% aqueous sodium hydroxide (532 ml.), and the mixture was heated with stirring either in an autoclave at 120° or on the steam bath. Samples were withdrawn at intervals and their carboxylic acid content determined as described below. Hydrolysis was 95% complete in 24 hours at 100° or in 6 hours at 120°.

Determination of Carboxylic Acid and Ester Groups in Modified NR

The concentrations of carboxylic acid and ester groups in the modified NR were determined as follows: (1) by comparison of the intensities of the bands at 1707 cm.⁻¹ (carboxyl) and 1730 cm.⁻¹ (ethyl ester) with those found at the same wave-

lengths for the monothioglycollic acid adduct of 2,6-dimethylocta-2,6-diene¹⁰ ($E_1^{1\%}$ = 38.3) and its ethyl ester ($E_1^{1\%}$ = 20.9); and (2) by volumetric analysis. The rubber carboxylic acid was allowed to stand in a solution of cyclohexylamine in benzene for 7 days at room temperature, when sufficient ethanol to precipitate all the rubber derivative was added. The excess of amine in the filtrate was estimated by titration with aq. 0.1*N* hydrochloric acid with bromophenol blue as indicator. The estimates given by method (2) were approximately 10% below those given by the first method.

Compounding and Vulcanization

The modified NR was compounded with the metallic bases and bis(2-hydroxy-3-*tert*-butyl-5-methyl phenyl)methane (Antioxidant 2246, American Cyanamid Co.) at room temperature on a small (6 × 2 in.) two-roll mill. Most of the vulcanizations were carried out with NR-ethyl thioglycollate and calcium hydroxide, and the standard procedure in this case was to compound the modified NR with the antioxidant (1% by weight calculation on the rubber) and a mixture of 3 moles of the hydroxide and 0.9 mole of propylene glycol per equivalent weight of ester (cf. ref. 3). The mixture of hydroxide and glycol was made by adding a solution of the glycol in 5 volumes of water to the powdered hydroxide (200 mesh), followed by drying at 50°C. to constant weight.

Vulcanization in press molds (to give 2-mm. sheets) was effected by heating at 150°C., usually for 1 hour. From the sheets were cut Type C British Standard 903 dumbbells or rings of external diameter 1.2018 cm. and internal diameter 1.018 cm.

Physical Testing

The stress-strain properties recorded in Figures 1, 2, and 5 (curve 1) were measured on a micro-scale rubber tensile tester¹¹ by extending the small rings at 600%/min. The stress relaxation properties recorded in Figure 3 were measured on a horizontal Hounsfield Tensometer (Tensometer Ltd., Croydon, England) by extending Type C British Standard 903 dumbbells to the required extension and then allowing the samples to relax. The creep properties recorded in Figure 4 and the stress-strain properties in Figure 5 (curve 3) were measured by attaching suitable weights to the Type C dumbbells. The stress-strain properties recorded in Figure 5 (curve 2) were also

measured on the horizontal Hounsfield Tensometer by extending the Type C dumbbells at 1 in./min.

Hydrolysis of the Ethyl Ester of Cyclohexylthioglycollic Acid with Calcium Hydroxide

A solution containing 20% by weight of the ester in paraffin (Nujol) was treated with an excess of the hydroxide for 1 hour at 140°C. Under these conditions only 4% by weight of the ester was hydrolyzed, but if water or propylene glycol (1 mole per mole of ester) were present, hydrolysis was almost complete (98%) in the same time. Only 2% hydrolysis occurred with water alone in 1 hour at 140°C.

Determination of the Extent of Hydrolysis Occurring during the Crosslinking of NR-Ethyl Thioglycollate with Calcium Hydroxide

The vulcanizate was cut into small pieces and allowed to stand in a mixture of benzene and *n*-butanoic acid until it dissolved (~2 days). This solution was then successively washed with water, dilute hydrochloric acid, and water until the washings were neutral and free from calcium ions. The rubber derivative was recovered from the organic layer by the addition of acetone, and, after thorough extraction with acetone and drying *in vacuo*, the carboxylic acid and ester groups were determined spectroscopically and volumetrically as described above.

RESULTS

Treatment of NR with Thioglycollic Acid and Its Esters

Treatment of dry NR or NR in solution, with thioglycollic acid, ethyl thioglycollate, and *n*-octyl thioglycollate gave the results recorded in Table II, all percentages quoted in the tables refer to moles of reagent used or combined per 100 isoprene units; addition efficiency is the ratio of thiol combined to that used.

The results show that the addition of the free acid is very inefficient. The esters were more reactive than the free acids, but even under the most favorable conditions addition was not as efficient as in latex (see below). Since the esters are more soluble in rubber than the free acid, the inertness of the latter would appear to be due mainly to its incompatibility.

TABLE II
Reaction of NR with Thioglycollic Acid and Its Esters (Catalyzed by AIBN)

Type of NR	Thiol compound	Thiol. concn., mole-%	Benzene concn., mole-%	AIBN concn., mole-%	Addition efficiency, %
Pale crepe	HSCH ₂ CO ₂ H	24.4	70	0.4	9
Pale crepe	HSCH ₂ CO ₂ Et	18.7	—	0.4	27
Pale crepe	HSCH ₂ CO ₂ C ₈ H ₁₇ ^a	21.7	700	2.6	35
Acetone-extracted pale crepe	HSCH ₂ CO ₂ H	48.0	70	1.0	17
Acetone-extracted pale crepe	HSCH ₂ CO ₂ Et	18.7	—	0.4	47

Treatment of NR Latex with Thiol Compounds— Mercapto Acids

Thiols react readily only with suitably stabilized and acidified latex^{9,12} (see Table IV). Thioglycollic acid, 11-mercaptoundecanoic acid, 2-mercaptooctanoic acid, and *p*-mercaptophenylacetic acid all failed to react with latex and frequently caused coagulation.

Esters of Mercapto Acids

These esters are only slightly soluble in water but readily soluble in rubber hydrocarbon, and they can be added to latex without causing coagulation. Table III shows the results obtained with several types of mercapto esters under the experimental conditions specified.

TABLE III
The Addition of Mercapto Esters to NR Latex^a

Ester	Addition efficiency, %
HSCH ₂ COOEt	91
HSCH ₂ COOBu ^a	85
HSCH ₂ COOC ₈ H ₁₇ ^a	75
HS(CH ₂) ₂ COOEt	48
HS(CH ₂) ₃ COOEt	13
HS(CH ₂) ₆ COOEt	8
HS(CH ₂) ₁₀ COOEt	5
HSC ₆ H ₄ COOMe	30
HSC ₆ H ₄ CH ₂ COOMe	53

^a Reactions were carried out for 7 days at 0° and at pH 1–2 using ester (13.6 mole-%) in benzene (28 mole-%) and *p*-menthane hydroperoxide (2.0 mole-%) as catalyst.

It can be seen from Table III that the ethyl, *n*-butyl, and *n*-octyl esters of thioglycollic acid add quite efficiently, and that the insertion of extra methylene groups between the two functional groups markedly reduces reactivity, so that the ethyl ester of 11-mercaptoundecanoic acid is

almost inert. The two aromatic esters added with moderate efficiency.

Treatment of NR Latex with Ethyl Thioglycollate

The effect of varying the pH, the reaction temperature, and the type of catalyst, on the reaction of ethyl thioglycollate with latex is shown in Table IV. From these results it is seen that: (1) addition is most efficient at pH 1–2; (2) free-radical catalysts are necessary, and their order of efficiency is hydroperoxides > ascaridole > AIBN; (3) with hydroperoxide catalysts addition is most efficient at low temperatures; and (4) less crosslinking occurs at lower temperatures.

Table V shows that the ester-modified rubbers of Table IV contain gel and sol fractions and that more ester was combined in the gel fraction. Crosslinking was much more severe with hydrogen peroxide than with *p*-menthane hydroperoxide. The sol products were separated into eight arbitrary fractions by the gradual addition of methanol to their solutions in benzene. From the analyses of the first and last fractions obtained from each sol product it can be seen (Table V) that all the sol products are heterogeneous, and that they become less heterogeneous if the reaction mixture is diluted with benzene.

NR-Thioglycollic Acid

Treatment of NR latex with ethyl thioglycollate gives a modified NR latex which can be hydrolyzed by hot sodium hydroxide. The carboxylic acid containing polymer so obtained is a rubber-like material, very similar in appearance to the parent NR-ethyl thioglycollate; it can be crosslinked by reaction with the oxides of zinc, cadmium, lead, and mercury. The above hydrolysis and the isolation of the NR-thioglycollic acid was not usually carried out since NR-ethyl thioglycollate can be directly hydrolyzed and crosslinked with divalent metallic hydroxides.

TABLE IV
The Addition of Ethyl Thioglycollate (8.5 Mole-%) to NR Latex

pH of NR latex	Catalyst (1.2 mole-%)	Reaction		Addition efficiency, %	Gel, % ^a	Gel swelling ^b
		Temp., °C.	Time, hr.			
9	<i>p</i> -Menthane hydroperoxide	20	72	0	—	—
6-7	<i>p</i> -Menthane hydroperoxide	20	72	45	—	—
1-2	<i>p</i> -Menthane hydroperoxide	20	72	76	—	—
1-2	None	60	24	2	—	—
1-2	AIBN	60	24	2	—	—
1-2	Ascaridole	60	24	18	—	—
1-2	<i>p</i> -Menthane hydroperoxide	60	24	34	—	—
1-2	Cumene hydroperoxide	60	24	38	—	—
1-2	Hydrogen peroxide ^c	60	24	46	—	—
1-2	<i>p</i> -Menthane hydroperoxide	60	24	34	90	13
1-2	<i>p</i> -Menthane hydroperoxide	20	24	70	81	18
1-2	<i>p</i> -Menthane hydroperoxide	0-5	24	89	31	36

^a Gel % is weight % of original rubber insoluble in benzene after immersion for 48 hours at 25°C.

^b Gel swelling is weight of swollen rubber/weight of de-swollen dry rubber, swelling carried out in benzene for 48 hours at 25°C.

^c Here, 6.0 mole-% hydrogen peroxide was used.

TABLE V
The Addition of Ethyl Thioglycollate to NR Latex

Ester concn., mole %	pH of latex	Catalyst	Catalyst concn., mole, %	Reaction		Benzene concn., mole-%	Addition efficiency, %	Gel, %	Combined ester, mole-%, in			
				Temp., °C.	Time, hr.				Gel, %	Total sol, %	First sol fraction	Last sol fraction
11.9	1-2	Hydrogen peroxide	5.0	0°	72	nil	85	91	11.2	5.3	—	—
11.9	1-2	<i>p</i> -Menthane hydroperoxide	1.0	0°	72	nil	56	10	10.0	6.6	3.4	14.3
11.9	1-2	<i>p</i> -Menthane hydroperoxide	1.0	0	72	70	62	50	8.9	6.9	4.6	9.2
11.9	1-2	<i>p</i> -Menthane hydroperoxide	1.0	0°	72	210	37	42	4.9	4.3	3.6	5.6

Crosslinking of NR Ethyl- Thioglycollate

Since hydrolysis is required before crosslinking of the ester can occur, wet metallic hydroxides and, in particular, calcium hydroxide in conjunction with propylene glycol³ were found to be much more efficient crosslinking agents than dry metallic oxides or hydroxides. The extent of hydrolysis was determined by treating the vulcanizate with an excess of *n*-butanoic acid, whereby all the calcium ions were removed as calcium butanoate and a soluble rubber produced in which the ester and carboxyl groups could be determined by the standardized methods.

The results obtained with a NR-ethyl thioglycollate (6.7 mole-% combined ester) vulcanized with calcium hydroxide at 150° are given in Table

VI. They show that hydrolysis is slow in the absence of propylene glycol but that it is almost complete in 1 hour in the presence of 0.9 mole

TABLE VI
Hydrolysis of NR-Ethyl Thioglycollates by Calcium Hydroxide-Propylene Glycol Mixtures at 150°

Hydroxide concn. mole/equiv. ester	Propylene glycol concn., mole/equiv. ester	Vulcanization time, hr.	Hydrolysis, %	
			Spectroscopic detn.	Volume metric detn.
3	—	0.5	12	—
1	0.3	0.5	22	17
3	0.9	0.5	46	48
5	1.5	0.5	92	82
7	2.1	0.5	100	92
3	0.9	1.0	96	—

of the glycol and 3 mole of the hydroxide per equivalent of ester. This mixture of hydroxide and glycol was adopted, therefore, as the standard vulcanization recipe for all NR-ethyl thioglycolates.

Physical Properties of NR-Ethyl Thioglycolates Crosslinked with Calcium Hydroxide

The NR-ethyl thioglycolates used for the investigation of physical properties were prepared from latex at 0°C. in the absence of solvent and with *p*-menthane hydroperoxide as catalyst. The modified rubber containing 6.7 mole-% combined ester contained 10% gel with a gel swelling of 32.

Effect of Drying on the Stress-Strain Properties

The stress-strain properties of a NR-ethyl thioglycolate (6.7 mole-% combined ester) vulcanized by the standard procedure and tested on the

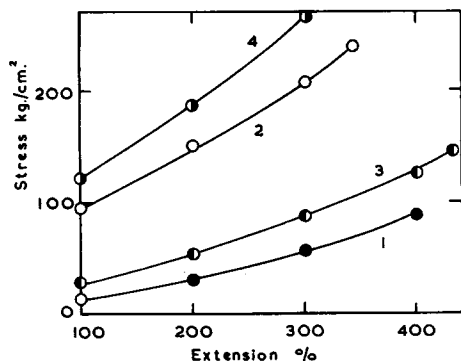


Fig. 1. Effect of water on the stress-strain properties of NR-ethyl thioglycolate (6.7 mole-% ester) vulcanized by the standard method, elongation at 600%/min.: (1) normal vulcanizate; (2) normal vulcanizate after drying; (3) dry vulcanizate treated with water; (4) wet vulcanizate re-dried.

microtensile tester¹¹ under the standard conditions (600% extension per minute) are shown in Figure 1 (tensile stresses are based on the original unstrained cross-sectional area). Curve 1 represents a typical undried vulcanizate and curve 2 is obtained when the vulcanizate is dried either by heating for 1 hour at 85° *in vacuo* or by standing for a few days in a desiccator over phosphorus pentoxide. It is seen that drying causes a considerable enhancement of the tensile properties of the material. If the dried vulcanizate (curve 2) is allowed to stand for one week in water at room temperature or for one day in steam at 100° then its properties deteriorate (curve 3), but the

original properties are regained if the wet vulcanizate is dried again (curve 4). The amount of water removed from the original vulcanizate by drying was 3.8% by weight.

Variation of Stress-Strain Properties with Extent of Modification

Figure 2 shows the stress-strain properties, measured by the standard procedure, of a series of dried vulcanized NR-ethyl thioglycolates (2.2–11.2 mole-% ester). Under these test conditions

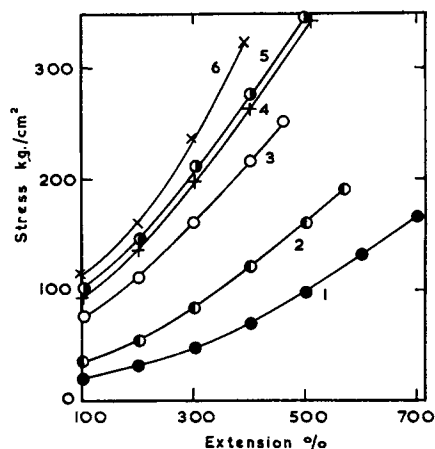


Fig. 2. Stress-strain properties of NR ethylthioglycolates vulcanized and dried by the standard methods, elongation at 600%/min.: (1) 2.2 mole-% combined ester; (2) 4.1 mole-% combined ester; (3) 5.6 mole-% combined ester; (4) 6.7 mole-% combined ester; (5) 8.7 mole-% combined ester; (6) 11.2 mole-% combined ester.

the vulcanizates from the two most highly modified rubbers have high tensile strengths and much higher moduli at 100% elongation than has a conventionally vulcanized NR, even when the latter contains an amount of carbon black corresponding to the amount of calcium hydroxide used to vulcanize the modified NR.

Stress Relaxation and Creep

Figures 3 and 4 show, respectively, the stress relaxation and creep of a vulcanized NR-ethyl thioglycolate containing 6.7 mole-% ester. Curve 1, Figure 3, was obtained at 20° and 150% extension and curve 2 at 70° and 300% extension, both with dried vulcanizates. It is seen that in both cases a linear stress-log time relationship is observed at first, but that eventually relaxation almost ceases before zero stress is reached. In Figure 4 a comparison is made of the creep at 20°

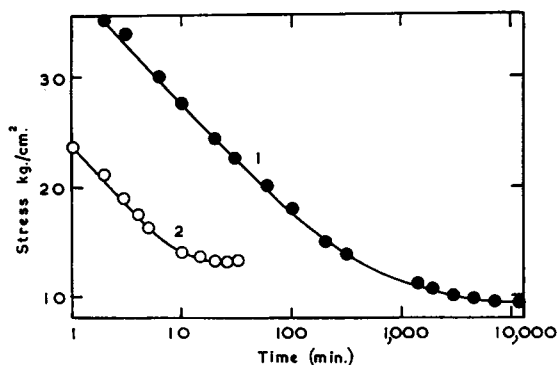


Fig. 3. Stress relaxation of NR-ethyl thioglycollates (6.7 mole-% ester) vulcanized and dried by the standard methods: (1) 150% elongation at 20° and (2) 300% elongation at 70°.

under an initial load of 20 kg./cm.² of the vulcanizate when wet (curve 2) and dry (curve 1). It is seen that the creep of the wet vulcanizate has almost ceased at about 400% elongation.

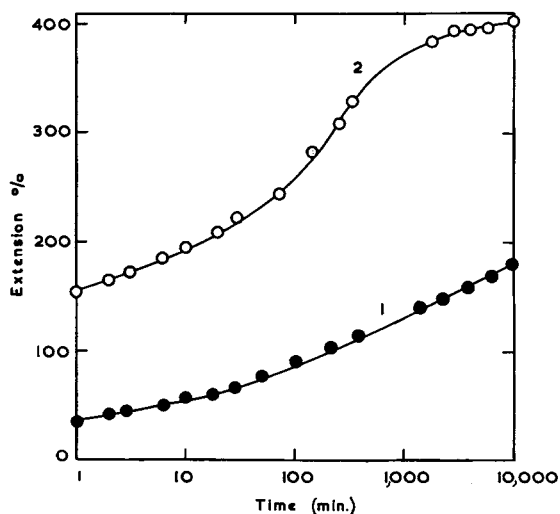


Fig. 4. Creep under stress (20 kg./cm.²) of NR-ethyl thioglycollate (6.7 mole-% ester) vulcanized by the standard method: (1) dried vulcanizate and (2) vulcanizate containing 8% of water by weight.

Variation of Stress-Strain Properties with the Rate of Extension

Under the normal conditions of testing; i.e., extension at 600%/min., high strength properties are obtained (Fig. 2). The rapid stress relaxation and creep shown in Figures 3 and 4 indicate that the stress-strain properties are markedly dependent upon the testing conditions, and Figure 5 shows the wide variation observed in stress-strain

properties of a vulcanized NR-ethyl thioglycollate (6.7 mole-% ester) at different rates of extension.

DISCUSSION

Preparation of the Modified Rubbers

Thiols are known to add readily to simple olefins,¹³ and to butadiene polymers and copolymers,¹⁴ but their addition to NR¹⁵ has not hitherto been accomplished efficiently. The results given here clearly show that although addition to dry rubber and rubber in solution is not very efficient, under suitable experimental conditions some mercaptoesters (and particularly those derived from thioglycollic acid) can be added efficiently to NR latex.

Course of the Reaction

The characteristic features of the reaction of ethyl thioglycollate with NR latex were previously outlined. The response to peroxide catalysis and the "abnormal" orientation of addition of thiols and thiol acids obtained from reactions with simple olefins in emulsion or in latex¹² indicates that combination of the thiol with NR proceeds via the free radical chain mechanism [reactions (1-6)], comparable with that proposed for the addition of *n*-butane thiol and benzene thiol to but-2-ene.¹⁶ The rapid reaction at low temperatures in the presence of hydroperoxides indicates that acidified latex activates this type of initiator (see also ref. 14). The small amount of cross-

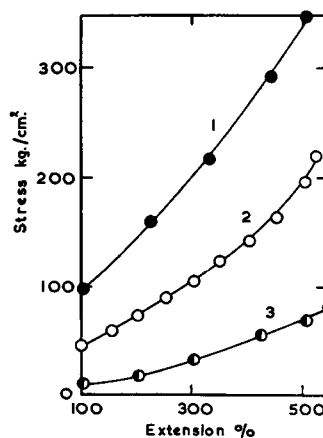


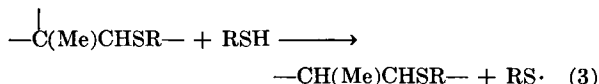
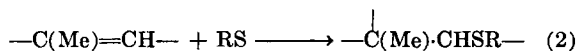
Fig. 5. Stress-strain properties at different rates of extension of NR-ethyl thioglycollate (6.7 mole-% ester) vulcanized and dried by the standard methods: (1) elongation at 600%/min.; (2) elongation at 200%/min.; (3) elongation at 2%/min.

linking which occurs presumably arises from the termination step (6):

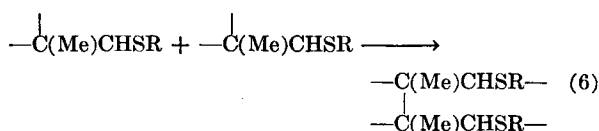
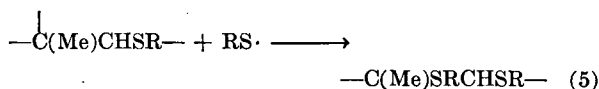
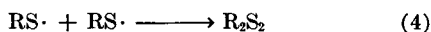
Initiation



Propagation



Termination



where R is EtCOOCH_2-

The degree of heterogeneity of the modified rubbers varied with the type of catalyst used and decreased as the amount of benzene used to dissolve the catalyst and the ethylthioglycollate was increased. Such heterogeneity presumably arises from reactions taking place preferentially on the surface of the latex particles; consistent with this is the fact that the water soluble catalyst hydrogen peroxide, gave the most heterogeneous products. A similar phenomenon has been reported in the preparation of graft polymers from methyl methacrylate and NR latex.¹⁷

Mechanism of Crosslinking

Natural rubber ethyl thioglycollates vulcanized by calcium hydroxide show marked creep under load, rapid stress relaxation at fixed extension, and marked sensitivity of their strength properties to the rate of extension and to water; features which contrast markedly with the physical properties of conventional rubber vulcanizates. Previous work² on the crosslinking of synthetic carboxylic acid polymers with metallic bases has indicated that the crosslink is a dibasic salt $-\text{COO}-\text{M}^{++}-\text{OOC}-$. The high strength and rapid stress relaxation of such vulcanizates was accounted for² by a mechanism of exchange between the electrovalent crosslinks on different chains whereby the network during extension avoids excessive local stress. This mechanism implies that the strained vulcanizate would eventually become completely

relaxed and that its permanent set would be large. The vulcanizates studied here exhibit efficient (although slow) elastic recovery (a sample extended to 250% for 1 hour had a permanent set of only 3% after 24 hours), and Figure 3 shows that stress relaxation ceases at a value indicating that the number of crosslinks remaining is comparable to that found in ordinary vulcanized rubber.

We suggest, therefore, that the divalent calcium salt crosslinks are relatively permanent and are responsible for the high elastic recovery of these vulcanizates and that their high modulus and tensile strength is mainly due to the presence of other ionic structures such as interactions between the crosslink sites which give the rubber a high internal viscosity. The variation of physical properties with testing conditions is typical of rubbers having high internal viscosity, and the effect of water could be due to its acting as a plasticizer between the ionic structures and so greatly lowering the internal viscosity of the rubber.

Further studies on the mechanism of this type of crosslinking and its effect upon the physical properties of the vulcanized polymer will be reported later.

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Synopsis

Mercapto acids do not react readily with dry natural rubber (NR), NR in solution, or NR latex, but some mercapto esters (mainly those derived from thioglycolic acid) have been added efficiently to latex and somewhat less efficiently to dry NR. The reaction between NR latex and ethyl thioglycollate has been examined in detail, and it has been found that addition proceeds efficiently at pH ~ 1 in the presence of hydroperoxide catalysts at 0°. The NR-ethyl thioglycollates so obtained are rubberlike materials which can be readily hydrolyzed and crosslinked. Calcium hydroxide in the presence of water or glycols is an effective crosslinking agent and the vulcanizates so obtained have physical properties typical of salt crosslinked polymers; i.e., their high tensile strengths and modulus properties are markedly dependant upon testing conditions.

Résumé

Les mercapto-acides ne réagissent pas rapidement avec le caoutchouc naturel sec, le caoutchouc naturel en solution, ou sous forme de latex; mais certains mercapto-esters (ceux dérivés principalement de l'acide thioglycolique) ont été ajoutés efficacement à du latex et un peu moins efficacement à du caoutchouc naturel sec. La réaction entre le caoutchouc

en latex et le thioglycolate d'éthyle a été étudiée en détail et on a trouvé que l'addition se produit efficacement à pH ~ 1 en présence de catalyseur hydroperoxydique à 0°. Les caoutchouc naturel-thioglycolates d'éthyle ainsi obtenus sont des matières caoutchouteuses qui peuvent être rapidement hydrolysées et pontées. L'hydroxyde de calcium en présence d'eau ou de glycols est un agent efficace de pontage et les vulcanisats ainsi obtenus ont des propriétés physiques typiques des polymères pontés sous forme de sels, c'est à dire, une haute résistance à la traction et des propriétés élastiques particulièrement dépendants des conditions expérimentales.

Zusammenfassung

Mercaptosäuren reagieren nur schwer mit trockenem Naturkautschuk (NR), mit NR in Lösung oder mit NR-Latex; einige Mercaptoester (hauptsächlich solche die sich von der Thioglykolsäure ableiten) wurden jedoch mit guter Wirkung dem Latex und mit etwas geringerer Wirkung dem trockenen NR zugesetzt. Die Reaktion zwischen NR-Latex und Äthylthioglykolat wurde genauer untersucht und es wurde gefunden, dass der Addition bei pH ~ 1 und in Gegenwart von Hydroperoxydkatalysatoren bei 0° in wirksamer Weise vor sich geht. Die so erhaltenen NR-Äthylthioglykolate sind kautschukähnliche Stoffe, die leicht hydrolytisch gespalten und vernetzt werden können. Calciumhydroxyd ist in Gegenwart von Wasser oder von Glykolen ein gut wirksames Vernetzungsmittel und die so erhaltenen Vulkanisate haben physikalische Eigenschaften, die für salz-vernetzte Polymere typisch sind, d.h. ihre hohe Zugfestigkeit und ihr Modul sind merklich von den Prüfbedingungen abhängig.

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