

Crosslinking Reaction of Rubber with Aldehydes

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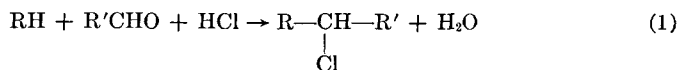
Synopsis

The reactions of rubber with aldehydes have previously been studied in latex or in solutions and the reaction products formed by cyclization, condensation, or addition, have been reported. In the present study, solid-state reactions of rubber with aldehydes were carried out. It was found that crosslinked rubbers may be obtained by press curing in the presence of aldehydes with acidic catalysts. Polychloroprene and Hypalon especially undergo these reactions without a catalyst or with a small amount of catalyst. In the experiments using various aldehydes, some improvements in the properties of the crosslinked rubber were observed when aldehydes such as paraformaldehyde or α -polyoxymethylene were used. Some Lewis acids such as $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were found to be more effective catalysts than the above, and it was found that organic acids such as *p*-toluenesulfonic acid could also be used. The curing seemed to be an ionic reaction. The physical properties of the crosslinked rubber are similar to these of sulfur-cured rubbers.

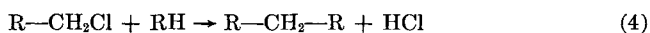
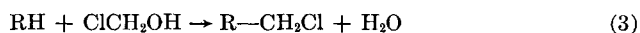
INTRODUCTION

Many workers have reported on the vulcanization of rubber. The majority of cases concern the vulcanization with sulfur.¹ Other curing agents and methods are also known, e.g., organic peroxide,² resin curing,³ oxime curing,⁴ and γ -irradiation curing.⁵ Cure systems for specific rubbers have been studied, i.e., metallic oxide for chloroprene rubber,⁶ metallic chloride for nitrile rubber,⁷ and metallic hydroxide for acrylic rubber.⁸ In general, there are two different mechanisms of curing: a free-radical mechanism and an ionic mechanism involving the carbonium cation. Although the crosslinking reaction of rubber is known to take place with aldehydes, the mechanism of the crosslinking reaction has not yet been clarified; it has however, been assumed to be an ionic reaction, involving formation of the carbonium cation by aldehydes in the presence of an acid. The reactions of rubber with aldehydes previously reported are concerned only with the reactions in latex or in solution, and the reaction with formaldehyde in the presence of acid. Adhesives⁹ and resinous materials¹⁰ have been obtained. In this work, various kinds and amounts of aldehydes and catalysts were mixed with various rubbers on a test roll mill, and the same crosslinked rubbers were obtained as in the case of the sulfur cure system.

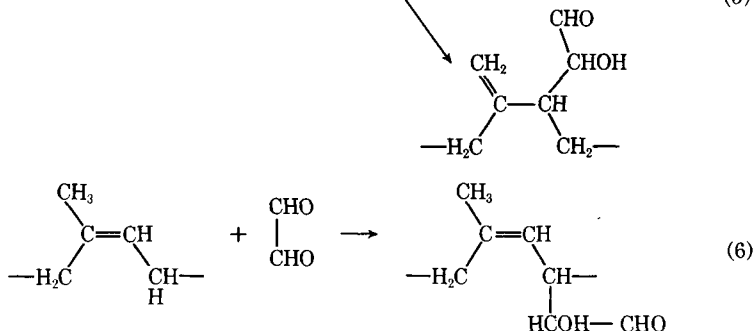
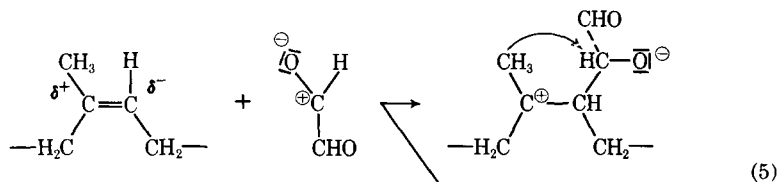
In the reaction of aldehydes with olefins, the Quelet reaction is known to be a basic reaction:



Saino¹¹ and Koide¹⁰ have reported on the reaction of a latex with formaldehyde in the presence of HCl. They obtained a reaction product, containing small amounts of chlorine, which gelled during the reaction. As a result, they assumed a crosslinking reaction caused by the reaction of the rubber with chloromethyl alcohol, formed by the reaction of formaldehyde with HCl, as shown by the eqs. (2)–(4).



In addition to the above products, olefinic alcohols are produced by the reactions of olefins with formaldehyde in the presence of the acid.¹² Concerning the addition reaction of aldehydes, e.g., chloral with *cis*-1,4-polyisoprene, Pinazzi¹³ has reported that the aldehyde which is directly attached to the main chain could readily undergo crosslinking between the molecules [eqs. (5) and (6)].



Thus, it is assumed that the crosslinking of rubber with aldehydes takes place first by the addition of methylol, followed by condensation of these adducts. Furthermore, Koide¹⁰ has indicated the possibility of cyclization due to the reaction of the unsaturated bond of the reaction product.

From another point of view, a copolymer having basic sites for the reaction with aldehydes will be capable of crosslinking. For example, the styrene of SBR has this reactivity toward aldehydes, although not many examples are known except for the chloromethylation of ethylbenzene¹⁴

and chloromethylation of β -chloroethylbenzene¹⁵ with formaldehyde in the presence of HCl and zinc chloride.

EXPERIMENTAL

Analysis of paraformaldehyde showed CH_2O , 96.2%; H_2O , 1.3%; Cl , <0.002%; SO_4 , <0.01%; Pb , <0.01; Fe , <0.001%. The trioxane, acetaldehyde, and aldehyde starch used were commercial reagents. The α -polyoxymethylene was supplied by the Sumitomo Bakelite Co. The $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and the other catalysts used were commercial reagents.

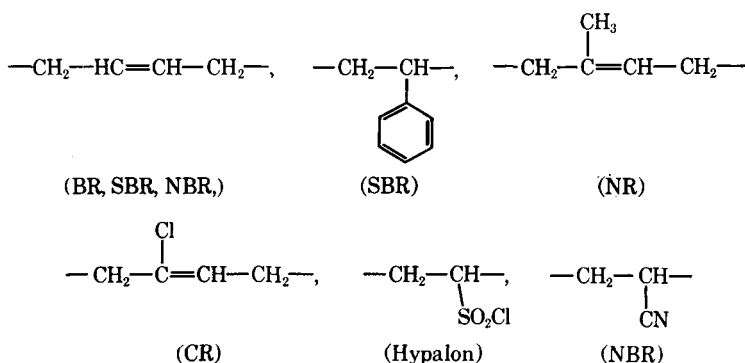
The rubber was masticated at temperatures between 40 and 50°C on a test roll mill, α -polyoxymethylene was added, and then the other ingredients were added. The catalyst was added last, and milling was carried out as fast as possible. The mixture was made into sheets 2 mm in thickness.

The rising time of the Mooney viscosity was taken as the initial cure rate of the rubber compound. After press cure at 150°C, the physical properties of the vulcanizate were examined according to the method of JIS K 6301, i.e., tensile strength, modulus, elongation, hardness, and tear strength. The apparent crosslinked network was determined by volume swelling in toluene.

RESULTS AND DISCUSSION

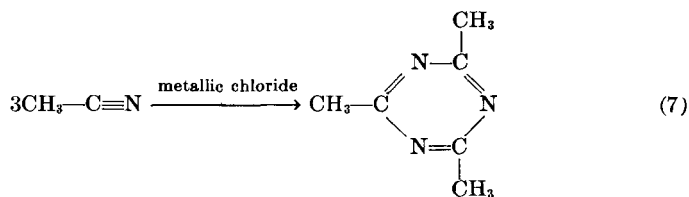
Types of Rubbers and Effect of Crosslinking

The crosslinking efficiency of the linear polymer is affected by the polarity of the main chain.



The cure of the polymers (BR, SBR, NR, CR, Hypalon, and NBR) was carried out with α -polyoxymethylene. The formulation and the results are given in Table I.

NBR was scorched during the mill mixing. It seems that, as illustrated by Zaharov,¹⁶ the CN group in NBR makes possible formation of crosslinks readily by a metallic chloride.



As shown in Table I, natural rubber (pale crepe no. 2), styrene-butadiene rubber (SBR 1013), high-styrene rubber (Hycar 2007), chloroprene (Neoprene WHV), and chlorosulfonated polyethylene (Hypalon 20) were cross-linked by α -polyoxymethylene in the presence of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

TABLE I
Cure Effects on Various Rubbers^a

Properties	Rubber				
	Pale crepe #2	SBR 1013	Hycar 2007	Neoprene WHV	Hypalon 20
Cure time, min	10	20	20	10	10
Hardness	66	86	98	90	86
100% modulus, kg/cm ²	28.7	45.9	—	46	77.9
300% modulus, kg/cm ²	94.1	90.8	—	134	—
Tensile strength, kg/cm ²	125.4	137.3	251.3	209	155
Elongation, %	384	495	10	499	188
Swelling in toluene, %	329	203	158	251	142
Abrasion loss, cc/HP hr	276	118	192	199	24.7
Resilience, %	22.4	16.7	19.0	20.0	13.6
Specific gravity	1.21	1.22	1.27	1.38	1.35

^a Formulation: rubber, 100 parts; α -polyoxymethylene, 10 phr; $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 10 phr; antioxidant, 1 phr; stearic acid, 1 phr; Nipsil VN-3 (hydrated silica), 58 phr. Cure: press cured at 150°C.

In order to obtain knowledge on the reactivity of paraformaldehyde and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ toward SBR, *cis*-1,4-polyisoprene (Cariflex 30), *cis*-1,4-polybutadiene (Cis 4) and chloroprene were mixed with paraformaldehyde and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, and the crosslinking efficiency of the stock was measured by means of the rising time of the Mooney viscosity at 121°C as given in Table II. The scorching characteristics of the diene polymers were observed in every case, but when these reagents were used together SBR showed a curing effect. Moreover, Hypalon and chloroprene rubber showed a self-catalyzing effect due to their acidic character, and accordingly these rubbers may be cured by aldehydes, as shown in Table III.

In regard to the effect of the addition of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ to halogenated rubber, chloroprene shows a strong self-catalytic action, and inferior physical properties of the vulcanizate were observed in the presence of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$; Hypalon, however, required a catalyst because of its weaker catalytic activity. Therefore, the crosslinking efficiency must be influenced by the acidity of the rubbers at the temperature of the cure. Consequently, it is

TABLE II
Reactivity of Paraformaldehyde and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ Toward Various Rubbers^a

Rubber	Paraformaldehyde, phr	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, phr	Mooney time at 121°C, min	Mooney viscosity
SBR 1013	8.2	—	>40	49.1
	—	5.0	>40	31.5
Cariflex 305	8.2	5.0	29.00	88.0
	8.2	—	2.70	
Cis 4	—	5.0	19.58	72.6
	8.2	5.0	<1	96.0
	8.2	—	1.50	
	—	5.0	3.67	
8.2	5.0	0.72		
Neoprene WHV	8.2	—	21.75	108.6
	—	5.0	<1	136.0
	8.2	5.0	<1	

^a Formulation: rubber, 100 parts; Nipsil VN-3, 58 phr; paraformaldehyde and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, variable.

TABLE III
Influence of Catalysts on Halogenated Rubbers

	Hypalon 20		Neoprene WHV	
Formulation				
Rubber	100	100	100	100
Paraformaldehyde	5	10	3	5
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	4	—	2	—
Nipsil VN-3	58	58	58	58
Cure				
Press cure time at 150°C, min	10	30	30	30
Properties				
Hardness (JIS)	90	80	85	82
100% modulus, kg/cm ²	153.9	24.7	32.8	35.7
300% modulus, kg/cm ²	—	35.4	85.1	105.2
Tensile strength, kg/cm ²	194	36	134.2	183.8
Elongation, %	139	416	599	545
Swelling in toluene, %	117	261	238	201
Specific gravity	1.30	1.28	1.40	1.37

clear that materials which become acidic on heating show self-catalytic action.

The results on crosslinking of polystyrene are shown in Table IV. The experiment was carried out to determine whether the phenyl group in SBR could be crosslinked with α -polyoxymethylene. Polystyrene was mixed with a curing agent in a mortar after blending polyisobutylene with polystyrene powder, and then the stock was cured at 150°C.

The results (Table IV) indicate that polystyrene may be cured through the phenyl groups, and this will be the same for SBR containing the

TABLE IV
Crosslinking of Polystyrene with α -Polyoxymethylene^a

Formulation					
Poly- styrene (Calinex GP), parts ^b	α -Polyoxy meth- ylene, phr	SnCl ₂ · 2H ₂ O, phr	Polyiso- butylene, phr ^c	Deformation at 160°C ^d	Swelling in benzene at 28°C
100	—	—	—	Melt	Soluble
100	20	—	5	Melt	Soluble
100	—	20	5	Melt	Soluble
100	20	20	5	No change	Insoluble

^a Cure: press cure for 20 min at 150°C.

^b Manufactured by Denk: Kagaku Kogyo Co., Japan.

^c Manufactured by Furukawa Kogaku Co., Japan.

^d Deformation on heating for 3 hr at 160°C after curing.

styrene units. However, the cure efficiency of the phenyl group was lower than that of the unsaturated double bond.

Aldehydes

After the observation of the curing character of paraformaldehyde for the various rubbers in the presence of SnCl₂·2H₂O, an experiment was carried out with various aldehydes. It was found that the mixing of liquid aldehydes such as CH₃CHO is very difficult for processing on the mill because of the softening of the rubber stock, as shown in Table V.

The most efficient aldehydes are α -polyoxymethylene and paraformaldehyde. The cure effect of higher aldehydes appears to be inferior to formaldehyde. In fact, Naunton¹² previously reported that lower aldehydes show a faster cure rate in the reaction of some olefins with aldehydes.

In compounding rubbers with various amounts of α -polyoxymethylene, the crosslink effects were examined (Table VI).

The Mooney viscosity of the compounded rubber decreased with increasing amount of α -polyoxymethylene. The physical strength of the vulcanizates was proportional to the increase in the amount of crosslinking agents, and the highest tensile strength was obtained with a formulation containing 7.6–11.6 phr of crosslinking agent with press cure at 145°C. With hot-air vulcanization, a higher strength of the vulcanizate was achieved than with the press cure (Fig. 1), in contrast to the lower strength in the case of the common sulfur vulcanizates.

On the other hand, the physical properties, such as the permanent set and the abrasion resistance, attained sufficient values when α -polyoxymethylene was used in amounts larger than 7.6 phr. In the absence of α -polyoxymethylene, the press-heated sheet did not show the appearance of a vulcanizate or a cyclizate.

TABLE V
Crosslinking Effects of Various Aldehydes^a

	Para- formaldehyde	α -Polyoxy- methylene	Trioxane ^b	Acetaldehyde ^c	Benzaldehyde ^e	Dialdehyde starch ^d
100% modulus, kg/cm ²	31.5	36.5	—	19.4	16.4	15.8
300% modulus, kg/cm ²	52.2	58.7	46.5	19.4	17.8	15.8
Tensile strength, kg/cm ²	151.1	148.9	67.2	19.4	18.0	15.8
Elongation, %	755	701	720	457	403	798
Swelling in toluene, %	295	303	451	256 ^e	368 ^e	248 ^e
Hardness (JIS)	82	80	78	76	74	70
Specific gravity	1.23	1.24	1.23	1.21 ^f	1.19 ^f	1.19 ^f

^a Formulation: SBR 1502, 100 parts, Nipsil VN-3, 58 phr; stearic acid, 2.0 phr; $\text{SnCl}_4 \cdot 2\text{H}_2\text{O}$, 10 phr; aldehyde, 10 phr unless otherwise noted.
Cure: press cured at 150°C for 30 min unless otherwise noted.

^b Trioxane content, 18.0 phr.

^c Cure time 75 min.

^d Cure time 90 min.

^e Dissolved a part of rubber stock in toluene.

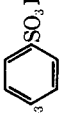
^f Containing bubbles in the rubber sheet due to under curing.

TABLE VI
Effect of α -Polyoxymethylene on Physical Properties of Vulcanizates^a

	Polyoxymethylene content, phr								
	0	1.4	2.8	3.8	5.4	7.6	11.6	15.2	
Mooney viscosity ML-4 at 100°C	—	91	85	83.3	74.7	81.5	74.5	72.7	
Mooney scorch time at 121°C, min	—	5.10	2.88	3.45	4.63	4.00	4.43	4.83	
Cure time, min	40	40	30	30	30	30	20	15	
Hardness (JIS)	64	78	82	82	84	82	82	72	
100% modulus, kg/cm ²	13.3	15.4	19.0	19.7	19.7	25.3	34.0	15.7	
300% modulus, kg/cm ²	14.0	29.4	37.4	41.4	41.4	52.0	55.6	37.4	
500% modulus, kg/cm ²	14.5	45.8	62.7	68.6	68.4	93.8	96.6	63.2	
Tensile strength, kg/cm ²	14.5	54.1	72.7	87.1	105.2	122.7	115.7	108.1	
Elongation, %	720	683	772	631	739	625	508	731	
Swelling in toluene, %	359	304	302	281	288	275	262	298	
Swelling in ASTM no. 3 oil, %	112	78.8	77.0	71.7	67.2	82.2	67.4	65.7	
Abrasion loss, cc/HP-hr	464	231	237	233	195	203	196	192	
Permanent set, %	—	71.2	65.0	42.5	37.5	32.5	26.3	30.0	
Tear strength, kg/cm	7	47	44	45	45	47	47	41	

^a Formulation: SBR 1013, 100 parts; Nipsil VN-3, 58 phr; stearic acid, 2.0 phr; SnCl₄·2H₂O, 5.7 phr; α -polyoxymethylene variable. Cure: press cured at 145°C.

TABLE VII
Cure Activity of Various Catalysts*

(PHR)	SnCl ₂ ·2H ₂ O (6.8 phr)	SnCl ₄ (7.94 phr)	AlCl ₃ (4.06 phr)	FeCl ₃ (4.94 phr)	ZnCl ₂ (4.2 phr)	KClO ₃ (3.16 phr)	HPO ₃ (2.99 phr)	 (5.78 phr)	Neoprene WHV (5.0 phr)	Chlorinated paraffin 40 (11.9 phr)
Color of uncured stock	White	Yellow	Brown	Black	White	White	White	Yellow	White	White
Processability of milling	Good	Scored on mill	Stuck on mill	Stuck on mill	Good	Good	Good	Good	Bad dispersion	Good
Mooney scorch time at 121°C, min	2.92		1.10	<1	15.50	2.50	15.00	0.67	>40	>40
Cure time, min	30		10	20	40	70	40	10	Uncured	Uncured
100% modulus, kg/cm ²	24.5		37.7	67.3	17.6	—	26.0	42.0		
300% modulus, kg/cm ²	46.3		—	—	—	—	26.2	78.0		
Tensile strength, kg/cm ²	124		43	97	18	9.7	29	110		
Elongation, %	595		149	262	168	153	365	530		
Tear strength, kg/cm	40		28	65	—	—	7.9	56		
Abrasion loss, cc/HP hr	466		186	37	—	—	274	204		
Permanent set, %	306		210	191	241	—	288	224		
Hardness (JIS)	80		86	86	74	70	74	88		

* Formulation: SBR 1502, 100 parts; Nipsil VN-3, 58 phr; stearic acid, 2.0 phr; paraformaldehyde, 8.2 phr. Cure: press cured at 150°C.

TABLE VIII. Effect of SnCl₂·2H₂O Content on Physical Properties of Vulcanizates^a

	α-POM = 3.8 phr			α-POM = 11.4 phr		
	SnCl ₂ ·H ₂ O, 1.4 phr	SnCl ₂ ·2H ₂ O, 2.8 phr	SnCl ₂ ·2H ₂ O, 4.4 phr	SnCl ₂ ·2H ₂ O, 5.7 phr	SnCl ₂ ·2H ₂ O, 8.8 phr	SnCl ₂ ·2H ₂ O, 11.4 phr
Mooney viscosity ML-4 at 100°C.	77.9	81.1	84.2	74.6	75.6	74.7
Mooney scorch time at 121°C, min	10.71	5.91	4.43	4.41	4.83	2.95
Optimum press cure time at 150°C, min	30	30	30	20	20	10
Hardness (JIS) 100% modulus, kg/cm ²	72	81	82	82	86	86
300% modulus, kg/cm ²	13.0	16.4	21.0	33.9	33.0	38.7
500% modulus, kg/cm ²	18.1	28.4	37.0	55.6	75.9	90.4
Tensile strength, kg/cm ²	27.3	42.7	60.9	96.6	—	—
Elongation, %	31.5	58.8	87.8	115.9	123.1	121.7
Swelling in tolu- ene, %	713	752	775	508	470	394
Swelling in ASTM no. 3 oil, %	324	322	298	262	226	210
Tear strength, kg/cm	86.6	78.1	68.1	48.2	49.3	43.5
Permanent set, %	14	35	43	44	43	47
Abrasion loss, cc/HP hr	111	56.2	47.6	26.3	21.3	22.5
	261	243	241	196	178	129

^a Formulation: SBR 1013, 100 parts; Nipsil VN-3, 58 phr; stearic acid, 2.0 phr; α-polyoxymethylene (α-POM) and SnCl₂·2H₂O variable.

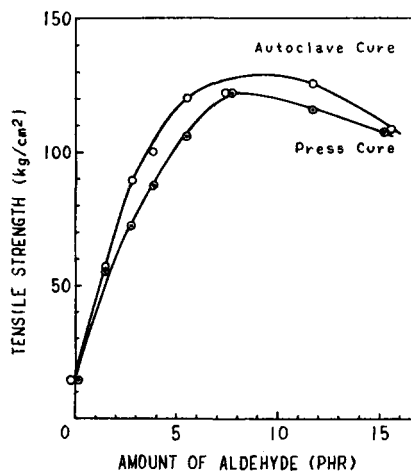


Fig. 1. Tensile strength vs. amount of aldehyde.

Cure Activity of Various Catalysts

Various kinds of catalysts were studied by using 8.2 phr paraformaldehyde with SBR 1502 (Table VII).

Equimolar amounts of catalyst and rubber were used. It was found that the SnCl_4 stock scorched in the roll-mill mixing, the AlCl_3 and FeCl_3 stock stuck on the roll mill surface during operation, the Neoprene and chlorinated paraffin 40 were not present in a sufficient amount for the cure; KClO_3 and H_4PO_3 have inferior effects on the physical strength, but they show an accelerating effect, and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and *p*-toluenesulfonic acid are good catalysts for the aldehyde cure system. These results show that the higher the acidity of the catalyst, the better the accelerating effect.

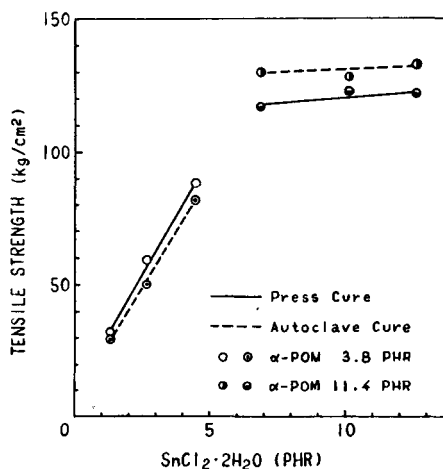


Fig. 2. Tensile strength vs. amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

Various amounts of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ were mixed in the stock with the use of α -polyoxymethylene as a crosslinking agent; the effects on the crosslinking reaction of the aldehyde were then studied. As shown in Table VIII, the amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was varied in the same rubber compounds.

It was found that the cure rate was influenced by the amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ rather than by the amount of α -polyoxymethylene. These compounds also showed the same highest strength of the vulcanizate in an autoclave cure as in the press cure. There was no delayed action even when oxygen was present, showing a good resistance to oxygen aging (Fig. 2).

The permanent set and tear strength approached a constant value near 5.7 phr $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. Especially in such an aldehyde cure as above, it is necessary to choose the catalysts from the point of view of the acceleration of the crosslinking reaction, instead of the cyclization reaction. The optimum ratio for the curing of SBR-hydrated silica stock was found to be 11.6 phr α -polyoxymethylene 8.8–11.4 phr $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

Influence of Fillers

Acidic fillers would appear to be suitable for reinforcing rubbers cured with aldehydes. Therefore, it is necessary to know the effect of the pH of the compounding fillers. Various fillers in quantities of 30 phr by volume were mixed with the rubbers and the crosslinking reaction of the stock was carried out. The physical properties of the vulcanizate were measured. This experiment also had the aim of finding the relationships between the physical properties and the particle sizes, and the difference in the effects of the fillers between carbon blacks and noncarbon fillers (Tables IX–XI).

The initial cure rates, as measured by the Mooney viscosity, increased with decreasing the pH of the carbon blacks and clays (Figs. 3 and 4).

It is a significant fact that paraformaldehyde readily changes to a carbonium cation in the presence of acidic fillers. Carbon blacks, which

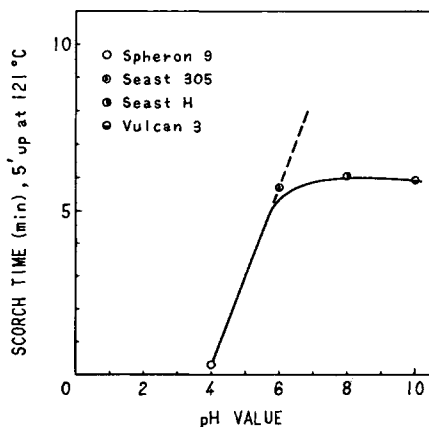


Fig. 3. Mooney scorch time vs. pH of carbon black.

TABLE IX
Properties of Fillers

Kinds filler type	Commercial brand	Manufacturer	pH	Particle size, m μ
Carbon black				
EPC	Spheron 9	Cabot	4.0	29
SRF	Gaston	Shiraishi	6.5	140
HAF	Seast 305	Tokai	6.0	35
"	"	Denkyoku		
"	"	"	8.0	35
"	Vulcan 3	Cabot	9.0	28
Hydrated silica				
Wet Process	Nipsil VN-3	Nippon silica	6.5	16
"	Carplex 1120	Shionogi	10.5	25-30
"	Tokusil GU	Tokuso	10.0	20-40
Clay				
Hard clay	Suprex clay	Hüls	5.0	<2000
Soft clay	Silkalite	Takehara	7.0	100-1000
Carbonates	Hakuenka C.C.	Shiraishi	9.5	20-40
CaCO ₃				
Precipitated	Calmos	"	9.5	40
CaCO ₃				
MgCO ₃	Tanmagu T	Tokuso	10.5	—
Diatomaceous earth		Mizusawa	6.0	—
Acid clay		"	6.5	—

TABLE X
Basic Formulation

	Parts
SBR 1502	100
Paraformaldehyde	10
SnCl ₂ ·2H ₂ O	10
Antioxidant ^a	1
Filler	30 ^b

^a Nonflex WS.^b Volume content, see Table XI.

contains active groups such as —OH, =O, —COOH, =CO, etc., on the surface of the particles, exhibited differences in behavior from those of clay and calcium carbonate fibers. As shown in Figure 3, those fillers having high pH values, i.e., Seast H and Vulcan 3, did not show any retarding action on the cure rate of rubber with aldehyde. The physical properties of the vulcanizates with various fillers are given in Table XII.

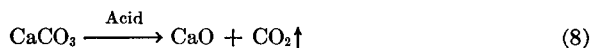
Acidic fillers were found to have reinforcing effects for the aldehyde cure. Carbon blacks and hydrated silica, especially, showed excellent effects.

TABLE XI
 Amount of Fillers*

Filler	Specific gravity	Content, phr
Spheron 9	1.8	54
Seast 305	1.8	54
Gaston	1.8	54
Seast H	1.8	54
Vulcan 3	1.8	54
Nipsil VN-3	1.95	58
Carpalex 1120	1.95	58
Tokusil GU	1.95	58
Suplex clay	2.65	78
Silkalite	2.65	78
Hakuenka CC	2.7	81
Calmos	2.6	78
Tanmagu T	2.2	66
Diatomaceous earth	2.6	78
Acid clay	2.6	78

* See Table X.

Calcium carbonates were poor fillers, forming a rubber foam when heated, probably because of the reaction (8):



In order to determine the reinforcing effect of hydrated silica, the amount of silica was varied, of 20, 40, and 60 phr, being used; the stocks were press cured at 150°C. The physical properties of the vulcanizates are shown in Figures 5-8 in which the properties of stocks vulcanized at the cure time which gives the maximum tensile strength are also shown for comparison.

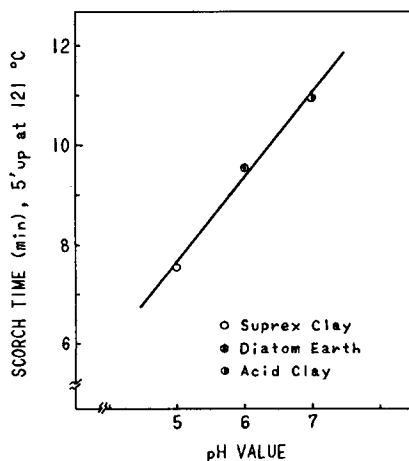


Fig. 4. Mooney scorch time vs. pH of clays.

TABLE XII. Physical Properties of Vulcanizates of Various Fillers^a

	Spheron 9	Seast 305	Gaston	Seast H	Vulcan 3	Nipsil VN-3	Suprex Clay	Silkalite	Dia- tomaceous earth	A clay
Cure time at 150°C, min	15	15	10	10	10	15	15	30	10	14
Hardness (JIS)	78	76	54	74	74	78	54	48	54	56
100% modulus, kg/cm ²	57.3	45.0	11.7	57.9	48.4	26	13	9	9.7	9.7
300% modulus, kg/cm ²	—	176	42.1	—	—	60	27.3	13.0	13.6	17.7
Tensile strength, kg/cm ²	111.1	183	106	138	144.1	140	62.5	17.0	22.6	21.0
Elongation, %	202	350	541	204	244	739	745	750	954	555
Swelling in toluene, %	164	175	242	200	177	249	332	721	402	467
Abrasion loss, cc/HP hr	29	27	466	27	72	73	814	1448	1002	922
Resilience, %	21.7	29.9	35.0	21.2	21.7	21.1	28.0	39.6	28.7	32.3
Specific gravity	1.17	1.18	1.18	1.16	1.17	1.21	1.29	1.29	1.29	1.28

^a Formulation as shown in Tables X and XI.

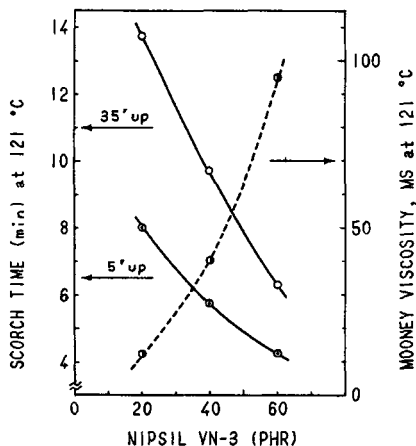


Fig. 5. Mooney scorch time and Mooney viscosity vs. amount of hydrated silica.

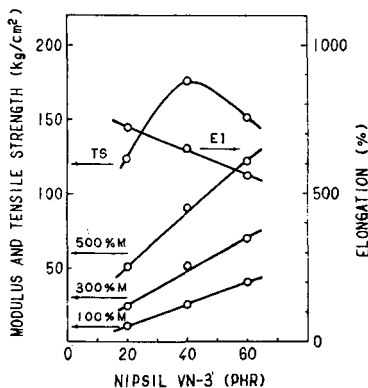


Fig. 6. Mechanical strength and elongation vs. amount of hydrated silica.

In the SBR compounding, hydrated silica had a promoting action for the aldehyde cure system. The increase in the modulus, tensile strength, and abrasion resistance of the vulcanizates, and the decrease in the degree of swelling in toluene were proportional to the increase in the amount of hydrated silica. The maximum tensile strength was obtained for the 40 phr compound. It was also observed that acidity and moisture may promote the crosslinking reaction. The aging of these vulcanizates is shown in Table XIII.

The results of hot air aging in a Geer oven at 100°C indicate that the compounded hydrated silica could prevent aging. Not even a slight reduction of mechanical strength was found to take place in the hot air vulcanization process.

Influence of Water

It is well known that a small amount of water in hydrated silica affects the sulfur cure system,^{17,18} i.e., the cure rate is increased and the physical

TABLE XIII. Aging in Geer Oven (100°C, 3 hr)

Nipsil VN-3 phr	Hardness (JIS)		100% modulus, kg/cm ²		Tensile strength, kg/cm ²		Elongation, %	
	Before aging	After aging	Before aging	After aging	Before aging	After aging	Before aging	After aging
20	64	+24	15.6	154	73.9	59	538	45
40	81	+14	20	134	147	63	698	37
60	85	+13	36.3	194	140	55	648	21

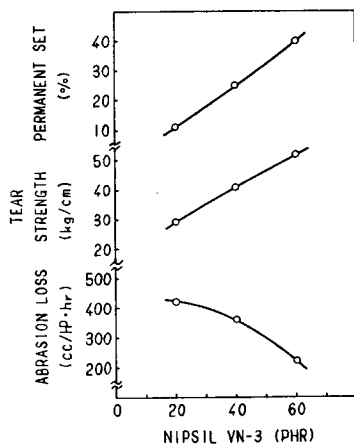


Fig. 7. Williams abrasion loss, tear strength, and permanent set vs. amount of hydrated silica.

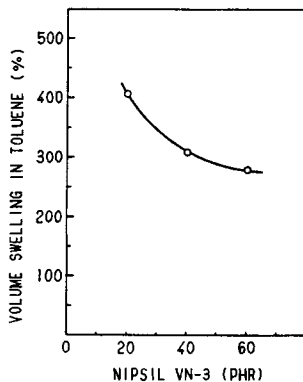


Fig. 8. Volume swelling in toluene vs. amount of hydrated silica.

properties change. It seemed that water in the aldehyde cure system would readily produce a carbonyl cation which has a curing activity for rubber. Experiments were therefore run in which the amount of distilled water was varied both in the carbon black stock and in the hydrated silica stock of the aldehyde cure system (Table XIV).

The water content of the hydrated silica and carbon black were measured, and water was added on the roll mill to make the water content a constant. The rate of cure was determined by the rising time of the Mooney viscosity at 121°C. The results given in Figure 9 show that the hydrated silica compound was not influenced by water, in contrast to the case of the carbon black compound. The following equations were obtained from Figure 9:

$$t_1 = 2.52 + 0.25W_{sc}$$

$$t_2 = 3.58 + 0.65W_{sc}$$

TABLE XIV
Water in Compound^a

Compound	Water in compound, g/100 g rubber	
	Hydrated silica ^b	Carbon black ^c
A	1.20	0.24
B	2.76	2.96
C	5.41	4.96
D	10.7	8.96
E	16.0	10.96
F	21.3	—

^a Formulation: SBR 1502, 100 parts; α -polyoxymethylene, 11.4 phr; $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 8.8 phr; stearic acid, 1.0 phr.

^b Nipsil VN-3, 60 phr.

^c Seast 305, 48 phr.

where t_1 and t_2 are the Mooney scorch times of hydrated silica (60 phr) and carbon black (48 phr) at 121°C , respectively, and W_{sc} is the water content in the stock. Assuming that T_1 and T_2 are the initial cure rates for each filler compound, the following relationships are obtained:

$$T_1 = 1/t_1$$

$$T_2 = 1/t_2$$

Water in the rubber stock delayed the initial cure rate of the aldehyde cure system, while in the case of the carbon black compound, the rate was slower than that of the hydrated silica compound. This is because of the activity of the filler particles. As shown in Tables XV and XVI, water delayed the crosslinking reaction of rubber with aldehyde, decreased the mechanical strength of the vulcanizates, and increased the swelling degree in toluene for the same cure time. These facts indicate that the addition of water may reduce the density of the crosslinking network. In contrast to the sulfur

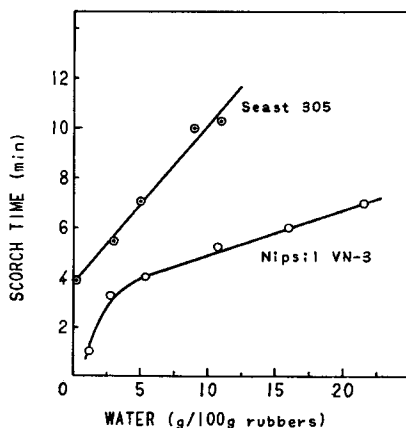


Fig. 9. Mooney scorch time vs. water content.

TABLE XV
Effect of Water in Carbon Black on Physical Properties of Vulcanizates

Properties	Water content, g/100 g rubber				
	0.24	2.96	4.96	8.96	10.96
Mooney viscosity ML-4	58	45	35	35	35
Press cure time at 155°C, min	40	40	30	40	30
300% modulus, kg/cm ²	165	160	150	125	120
Tensile strength, kg/cm ²	210	222	215	196	190
Elongation, %	375	380	425	455	458
Hardness	70	70	70	70	70
Tear strength, kg/cm	40	40	45	48	48
Resilience, %	44	43	43	43	42
Abrasion loss, cc/HP hr	9.3	9.5	11.4	21.5	20.1
Swelling in toluene, %	350	352	370	382	393

TABLE XVI
Effect of Water in Hydrated Silica on Physical Properties of Vulcanizates

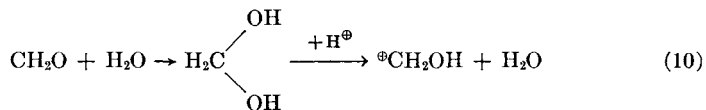
Properties	Water content, g/100 g rubber					
	1.2	2.76	5.41	10.7	16.0	21.3
Mooney viscosity ML-4	158	140	135	128	110	75
Press cure time at 155°C, min	20	10	20	40	60	60
300% modulus, kg/cm ²	140	93	80	60	43	28
Tensile strength, kg/cm ²	181	185	201	165	152	133
Elongation, %	455	603	690	710	885	890
Hardness	88	82	85	81	80	76
Tear strength, kg/cm	56	55	60	65	57	50
Resilience, %	35	36	37	38	39	40
Abrasion loss, cc/HP hr	14.0	14.8	17.5	24.0	28.0	—
Swelling in toluene, %	218	235	251	278	310	318

cure system, water in the aldehyde cure system decreased the cure rate and produced an inferior mechanical strength of the vulcanizates.

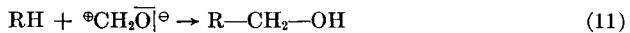
Mechanism of Crosslinking

The crosslinking of rubber with aldehydes in the presence of an acidic atmosphere was studied, and a new crosslinking method for rubber was found. The crosslinking reaction in this cure system was not fully clarified, however. The reaction may be initiated by the formation of a carbonium cation from formaldehyde in the acidic atmosphere. There seem to be two

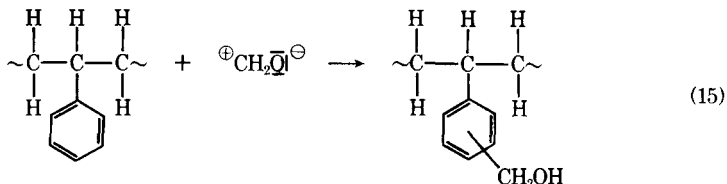
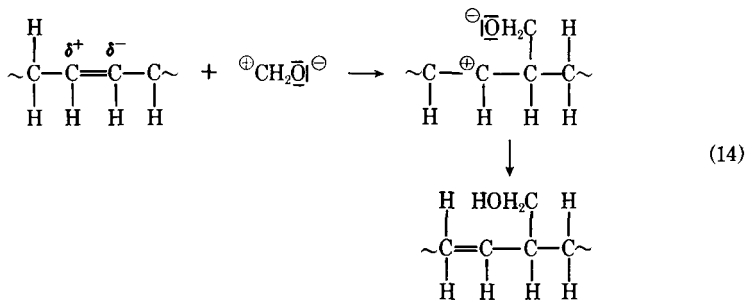
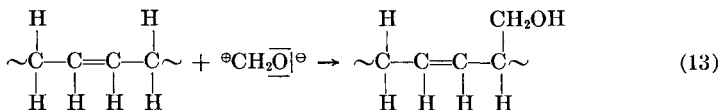
cases for the formation of the carbonium cation, as shown in eqs. (9) and (10).



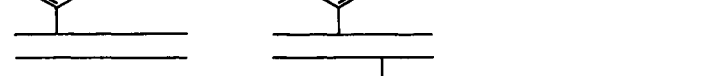
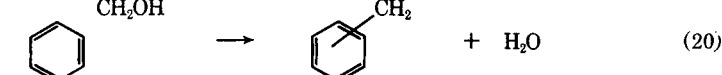
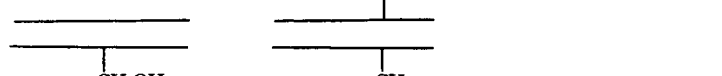
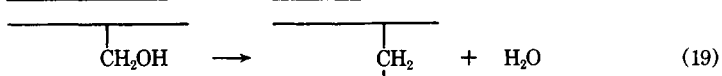
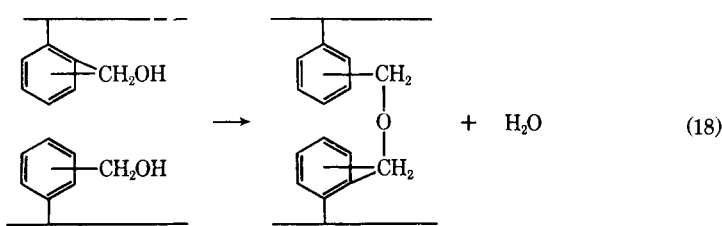
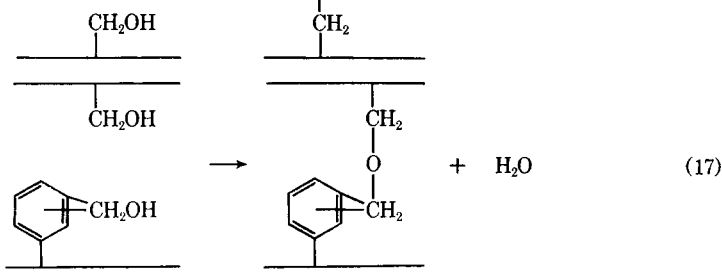
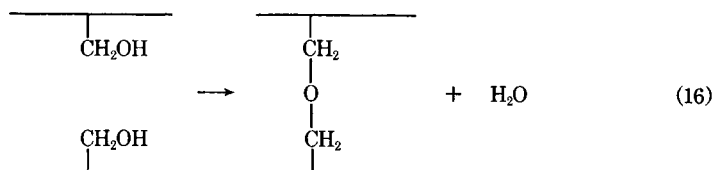
The carbonium cation adduct rubber (RH) is formed, and then a methylol derivative of rubber is obtained [eqs. (11) and (12)].



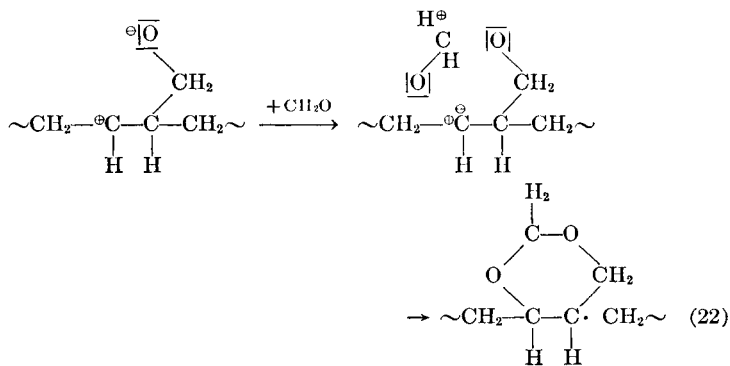
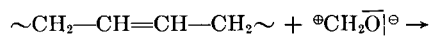
The carbonium cation will add directly to the active α -carbon [eq. (13)] or to the polarized double bond, thus forming a new double bond in the adjacent bond [eq. (14)]. When SBR was used, the carbonium cation attacks the phenyl group of SBR [eq. (15)] as predicted above.



The adduct of the methylol group to rubber was dehydrated in the presence of acid on heating [eqs. (16)–(18)]. At the same time, dehydration may take place between the methylol group and the rubber hydrocarbon as shown by eqs. (19)–(21). Thus, crosslinked rubber would be obtained. (In these equations the straight chain denotes the rubber.)



However, the reaction might proceed by the Prins reaction [eq. (22)] to form *m*-dioxane.



CONCLUSIONS

Reactions of bulk rubber with aldehydes were carried out. It was found that crosslinked rubber is obtainable by press curing in the presence of aldehydes with acidic catalysts. The rubbers obtained by the above method have properties similar to those of sulfur-cured rubbers. The following conclusions were reached.

(1) Natural rubber, SBR, high-styrene rubber, chloroprene, and Hypalon can be crosslinked by aldehydes on heating in the presence of acidic compounds. Rubbers which exhibit acidity on heating, e.g., chloroprene and Hypalon, showed an autocatalytic action. The phenyl group in SBR may be crosslinked.

(2) The most efficient aldehydes were the series of formaldehyde, e.g., paraformaldehyde and α -polyoxymethylene.

(3) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and *p*-toluenesulfonic acid are effective catalysts for the aldehyde cure. Optimum contents of α -polyoxymethylene and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ SBR-hydrated silica stock were found to be 11.6 phr and 8.8 – 11.4 phr, respectively.

(4) Acidic fillers were found to make the cure faster and to give excellent physical properties to the vulcanizates. Basic fillers, except for active carbon black, interfered with the crosslinking reaction for the aldehyde cure system.

(5) The mechanism of the crosslinking may proceed as follows in the presence of acids on heating: formaldehyde first forms a carbonium cation, then the carbonium cation attacks the rubber to form a methylol derivative of rubber. The methylol group reacts with another methylol group or with rubber to split off water and thus forms a crosslink.

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