

Vulcanization with Maleimides*

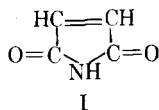
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Synopsis

Series of mono- and bismaleimides were evaluated as curing agents to determine the effect of structure on crosslinking ability. The activity of *N*-phenylmaleimide derivatives (monomaleimides) as crosslinking agents is highly dependent upon the substituent on the phenyl group. The activity of bismaleimides is likewise affected by the nature of the moiety connecting the maleimide rings. Isomaleimides and itaconimides are less effective curatives. Initiators for the maleimide cures include peroxides and sulfur accelerators of the thiazole type. Saturated and unsaturated hydrocarbon rubbers, except those containing a high percentage of isobutylene units, are vulcanized by a maleimide-initiator system. One of the attractive features of a maleimide curing system is that the physical properties of the cured rubbers are independent of curing temperature. Further, these vulcanizates have the good aging characteristics typical of nonsulfur-cured vulcanizates. In contrast to sulfur vulcanization, the maleimide curing systems do not markedly affect the ability of elastomers to crystallize when stretched. Therefore, the T_{50} test cannot be used to assess the state of cure of maleimide-natural rubber vulcanizates. Maleimides containing an appropriate second functional group can be used as self-accelerating curing agents or as adhesives.

Introduction

During the course of an extensive study of the chemistry of maleimide (I) and its derivatives,^{1,2} it was found that many maleimides not only readily

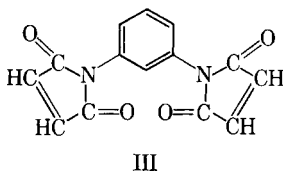
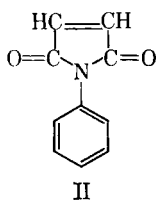


copolymerize with vinyl monomers, but also cure rubber in the presence of suitable initiators. This maleimide cure of rubbers has also been studied independently by Kovacic and others.³⁻⁷ We have found that substituted maleimides such as II and III produce vulcanizates which generally have

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better heat- or air-aging properties than the corresponding sulfur-cured stocks. Therefore, the scope and limitations of the maleimide curing system were examined and the aging properties of the vulcanizates were determined to establish more fully the usefulness of maleimide-based curing agents.

Scope and Limitations

We have confirmed the observations of Kovacic and Hein³ that bismaleimides are much more effective than monomaleimides as curing agents and that a promoter such as a peroxide is required for best results. Additionally it has been found that MBTS (2-benzothiazolyl disulfide) is an effective promoter of the maleimide cure. Properties of styrene-butadiene rubber (SBR) stocks cured by a monomaleimide and a bismaleimide are compared in Table I.

TABLE I
Comparison of Mono- and Bismaleimide Cures

Composition, parts					
Styrene-butadiene (24:76) copolymer	100	100	100	100	100
High-abrasion furnace black	50	50	50	50	50
Heavy paraffin oil	7.5	7.5	7.5	7.5	7.5
N-Phenylmaleimide	4.0	4.0	4.0		
<i>N,N'</i> - <i>m</i> -Phenylenedibismaleimide				0.85	0.85
MBTS		2.0		2.0	
Dicumyl peroxide, 40% active, on CaCO ₃ (Hercules Powder Co.)			0.7		0.7
Cured 22 min. at 309°F.					
Properties					
Tensile strength, psi	275	2730	2535	2405	2085
Breaking elongation, %	480	490	450	460	500
Stress at 300% elongation, psi	175	1285	1250	1125	1025

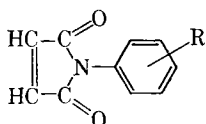
It can be seen from Table I that nearly the same state of cure results from using only 6.5 mmoles of combined maleimide groups/100 g. of rubber in the form of the bismaleimide as from 23 mmoles of combined maleimide groups/100 g. of rubber in the form of the monomaleimide.

A large number of mono- and bismaleimides was prepared and tested in SBR to determine the effect of structure on curing activity. The structures and properties of the monomaleimides are listed in Table II. The ultra-

violet and visible spectra of the monomaleimides show that there is an electronic interaction between the maleimide and phenyl rings, since the absorption maxima appear at longer wavelengths than in the spectra of either maleimide itself or the corresponding benzene. Therefore, the electron-releasing or withdrawing effect of a substituent on the benzene ring is transmitted to the maleimide ring. Table II shows that, in general, a higher electron density in the maleimide ring leads to greater activity as a curing agent. The low modulus found for SBR cured with 4-methylphenylmaleimide probably results from the poor solubility of the curing agent in rubber as evidenced by blooming. 2,6-Dimethylphenylmaleimide gave a surprisingly low modulus. However, molecular models of this curative show that the two methyl groups twist the phenyl and maleimide rings out of coplanarity and therefore electron-release by resonance from the benzene ring to the maleimide group is impossible. The net result is that 2,6-dimethylphenylmaleimide is about as poor a curative as 2- or 3-nitrophenylmaleimide, in which there is a strong electron-withdrawing group.

The curing activity of bismaleimides is also dependent on structure, for the bridging group which joins the maleimide rings has a strong influence as shown in Table III. Activity does not correlate with structure as obviously as in the case of the monomaleimides and may be partly dependent upon solubility of the curing agent in rubber.

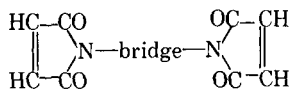
TABLE II
Monomaleimide Curing Agents



R	λ_{\max} (hexane)	Color	Stress at 300% elongation, psi ^a
4-Ethoxy	347	Yellow	1480
4-Methoxy	345	Yellow	1515
4-Methyl	336	Yellow	925
3-Methyl	322	Yellow	1450
Hydrogen	321	Yellow	1425
3-Chloro	318	Light yellow	1300
2-Naphthyl	312	Yellow	1210
2-Chloro	297	White	1150
2-Methyl	296	White	1125
2,4-Dimethyl	295	Yellow	1175
2,5-Dichloro	294	White	300
3-Nitro	292	White	730
2-Nitro	288	White	725
2,6-Dimethyl	287	White	725
4-Nitro	—	White	580

^a For SBR containing 50 phr of a fast-extrusion black, cured 45 min. at 331°F. with 100 phr of *N*-phenylmaleimide or equivalent and 2 phr of 2-benzothiazolyl disulfide.

TABLE III
Bismaleimide Curing Agents

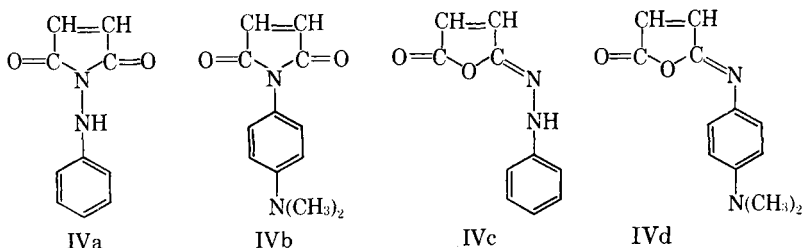


Bridge	Stress at 300% elongation, psi ^a
4,4'-Methylenediphenyl	(1875) ^b
<i>m</i> -Phenylene	1475
4-Methyl- <i>m</i> -phenylene	1475
4,4'-Ethylenediphenyl	1050
4,4'-Vinylenediphenyl	950
None	950
2,2'-Dithiodiphenyl	925
<i>p</i> -Phenylene	900
4,4'-Biphenyl	850
4,4'-Ethylenebis(oxyphenyl)	850
<i>o</i> -Phenylene	700
4,4'-Sulfonyldiphenyl	600
3,3'-Dichloro-4,4'-biphenyl	500
—CH ₂ OCH ₂ —	(500) ^b
3,6-Durylenebisethylene	250
3,6-Durylene	200
—CONH(CH ₂) ₆ NHCO—	No cure

^a Measured on stocks prepared from styrene-butadiene rubber, with 40 phr of a high-abrasion furnace black, 7.5 phr of heavy paraffin oil, 2.0 phr of *N,N'*-phenylenebismaleimide or equivalent and 1.0 phr of di-2-benzothiazolyldisulfide; cured 45 min. at 307°F.

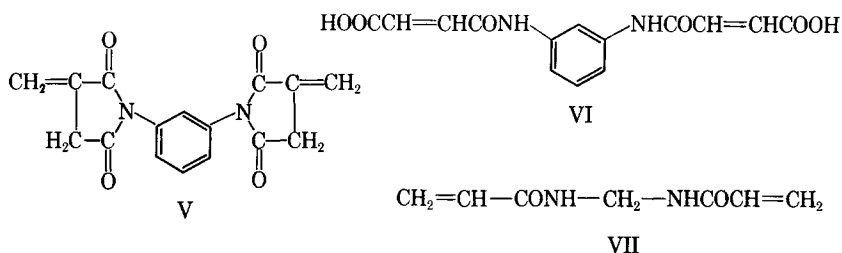
^b Extrapolated.

Attempts to prepare monomaleimides having the powerful electron-releasing substituents *N*-anilino- (IVa) or *N*-(4-dimethylaminophenyl)- (IVb) led instead to the corresponding isomaleimides (IVc, IVd). The



structures of these compounds were established by nuclear magnetic resonance spectroscopy. The isomaleimides were found to have no curing activity in SBR with either dicumyl peroxide or di-2-benzothiazolyl disulfide (MBTS) accelerator.

Several other types of compounds related to maleimide were found to possess moderate curing activity. These are bisitaconimides (V), the



open-chain compounds of the bismaleamic acid type (VI), and *N,N'*-methylenebisacrylamide (VII). The data in Table IV show that none of

TABLE IV
Vulcanization with Itaconimides and Open-chain Compounds Related to Maleimide

Composition				
Styrene-butadiene (24:76) copolymer	100	100	100	100
High abrasion furnace black	40	40	40	40
Heavy paraffin oil	7.5	7.5	7.5	7.5
<i>N,N'</i> - <i>m</i> -Phenylenebisitaconimide	2.2			
<i>N,N'</i> -Methylenebisacrylamide		1.4		
<i>N,N'</i> - <i>m</i> -Phenylenebismaleamic acid			2.3	
<i>N,N'</i> - <i>m</i> -Phenylenebismaleimide				2.0
Dicumyl peroxide, 40% active, on CaCO ₃ (Hercules Powder Co.)	1.0	1.0	1.0	1.0
Cured 90 min. at 309°F.				
Properties				
Tensile strength, psi	2050	1740	2020	2140
Breaking elongation, %	440	410	520	250
Stress at 300% elongation, psi	1175	1025	900	(2600)*

* Extrapolated.

these compounds is as effective as *m*-phenylenebismaleimide used at the same molar equivalent level.

It has already been mentioned that both dicumyl peroxide (as found by Kovacic and Hein)³ and MBTS accelerate the maleimide cure. Several other accelerators known to promote sulfur cures were also tried with both mono- and bismaleimides. The results shown in Table V demonstrate that the sulfenamide accelerators 2-(morpholiniothio)benzothiazole and *N*-cyclohexyl benzothiazole sulfenamide are effective, although not quite as good as di-2-benzothiazolyl disulfide. 2-Mercaptothiazoline does not promote cures by either mono- or bismaleimides.

Several other saturated and unsaturated rubbers were tested for curability by maleimides. The results given in Table VI show that all except butyl rubber cure readily under conventional conditions (times of 15–90 min., temperatures of 287–320°F.).

TABLE V
Activity of Accelerators in Maleimide Cures

Composition, parts								
Styrene-butadiene (24:76) copolymer	100	100	100	100	100	100	100	100
Fast-extrusion black	50	50	50	50	50	50	50	50
Heavy paraffin oil	8	8	8	8	8	8	8	8
<i>N</i> -Phenylmaleimide	4	4	4	4				
<i>N,N'</i> - <i>m</i> -Phenylenebismaleimide					1.1	1.1	1.1	1.1
MBTS	2				2			
2-(Morpholiniothio)benzo- thiazole		2				2		
<i>N</i> -Cyclohexyl benzothiazole sulfenamide			2				2	
2-Mercaptothiazoline				2				2
Cured 45 min. at 307°F.								
Properties								
Tensile strength, psi	2860	2940	2460	120	2630	2130	1500	40
Breaking elongation, %	480	590	710	1290	440	590	650	800
Stress at 300% elongation, psi	1325	990	575	75	1400	775	465	50

TABLE VI
Cures of Saturated and Unsaturated Rubbers by *m*-Phenylenebismaleimide and
Accelerator

Composition, parts								
Ethylene-propylene (1:1) rubber		100						
Ethylene-propylene adipate modified with 4,4'-methylenediphenyl iso- cyanate and allyl alcohol			100					
Styrene-2-methyl-5-vinylpyridine-bu- tadiene (12:12:76) copolymer				100				
Butadiene-acrylonitrile copolymer					100			
Polychloroprene							100	
Isobutylene-isoprene copolymer								100
Fast-extrusion black		50	22.4			35	35	
Medium-processing channel black				50				40
<i>N,N'</i> - <i>m</i> -Phenylenebismaleimide		3	5		2.5	3	1.3	3
MBTS					2		1	
Dicumyl peroxide, 40% active, on CaCO ₃ (Hercules Powder Co.)			4	1			0.8	2
Cure conditions								
Time, min.		15	60	90	30	30	90	
Temperature, °F.		320	287	292	307	307	307	
Properties								
Tensile strength, psi		1910	3090	2350	2400	2015	250	
Breaking elongation, %		380	420	540	470	390	1010	
Stress at 300% elongation, psi		1350	1900	875	1530	1200	60	

High Temperature Vulcanization with Maleimides

It is apparent that the output of curing operations can be increased by raising the curing temperature. In the tire industry, press cycles of the

order of 15–25 min., with temperatures up to 390°F., are used for passenger tires. However, a reduction of tire curing times with conventional sulfur curing systems is limited, because further increases in temperature reduce the quality of the product. Juve and Garvey⁸ as well as Svetlick and Railsback⁹ found that the physical properties of sulfur-cured SBR stocks are adversely affected by increasing the curing temperature over the range of 250–350°F. Smith¹⁰ reported that increases in the curing temperature in the range 292–500°F. exert a deleterious effect on sulfur-cured natural rubber, SBR, neoprene, and butyl. The magnitude of the effect varies for each elastomer and can be largely prevented by selecting a proper curing system for polymers like natural rubber or butyl which revert at the higher curing temperatures.

In contrast with a sulfur curing system, a maleimide curing system is very attractive for high temperature cure applications. The maleimide vulcanizates are heat-stable, and there is no reversion reaction occurring simultaneously and in competition with the crosslinking reaction at high temperatures. Therefore, a maleimide curing system used in very short curing cycles at high temperatures gives vulcanizates with properties which are essentially equal to those obtained in longer cycles at lower temperatures.

A carcass stock of SBR, natural rubber and reclaim was vulcanized with sulfur and N-cyclohexyl benzothiazole sulfenamide as well as with a bismaleimide (*m*-phenylenebismaleimide) and dicumyl peroxide. The curing conditions selected for both stocks are shown in Table VII. The conditions shown are not to be considered as an equivalent cure series. The precise control of the cure time at the higher temperatures is impossible because of mold lag and the equipment used.

TABLE VII
Curing Conditions for Carcass Stocks

Time of cure, min.	Temp. °F.
30 and 60	300
4, 8 and 16	350
1, 2, 3 and 4	400
1, 2, 3 and 4	450

Since the stocks did not revert, the values of the physical properties measured at each temperature were averaged over all cure times. The average tensile strength, stress at 300% elongation, breaking elongation, hardness and torsional hysteresis for both stocks at each curing temperature are given in Table VIII.

These results show that the tensile strength, stress at 300%, and hardness of the sulfur carcass stock are reduced at higher curing temperature, while the torsional hysteresis has increased. The properties of the bismaleimide carcass stock, cured during a short cycle at the high temperature, are es-

TABLE VIII
Physical Properties of a Carcass Stock, Vulcanized with Sulfur and Accelerator or Bismaleimide and Peroxide at Different Temperatures

Property	300°F.	350°F.	400°F.	450°F.
Tensile strength, psi				
Sulfur	1870	1610	1330	920
Bismaleimide	1520	1530	1475	1350
Breaking elongation, %				
Sulfur	465	470	420	355
Bismaleimide	390	360	380	340
Stress at 300%, psi				
Sulfur	1110	860	781	685
Bismaleimide	1015	1030	1040	1010
Hardness, Shore A				
Sulfur	55	51	51	46
Bismaleimide	50	49	48	48
Torsional hysteresis at 285°F.				
Sulfur	0.123	0.130	0.153	0.162
Bismaleimide	0.153	—	0.145	0.137

essentially equal to those obtained during the longer curing cycles at lower temperatures.

The stability of bismaleimide vulcanizates at high curing temperature can be even better demonstrated with natural rubber. In Table IX, the properties of sulfur and bismaleimide (*N,N'*-*m*-phenylenebismaleimide) natural rubber vulcanizates, cured at different temperatures and times, are given. Sulfur-cured natural rubber will revert during long curing times at lower temperatures and vulcanizates cured during short times at high temperature do not have the same properties as vulcanizates cured at the lower temperatures. However, the bismaleimide natural rubber vulcanizates cured at low or high temperature have essentially the same properties and do not revert, even during longer curing times at high temperature.

A monomaleimide curing system is not only less active as a crosslinking agent, but also the vulcanizates obtained with the monomaleimides are less heat-stable than the bismaleimide vulcanizates. Table X shows that the properties of the monomaleimide-natural rubber vulcanizate decrease more rapidly with an increase in curing temperature than do the properties of a bismaleimide-natural rubber vulcanizate.

Air Aging of Maleimide Vulcanizates

A maleimide curing system not only gives heat-stable vulcanizates but also vulcanizates which are less susceptible to attack by oxygen. The sulfur crosslink makes hydrogen atoms on the carbon atoms attached to the sulfur susceptible to oxidation. Obviously with a bismaleimide curing system this activation by sulfur is not possible.

Stress relaxation curves obtained in air at 230°F. for natural rubber cured either with sulfur and an accelerator or with a bismaleimide initiated with

TABLE IX
Properties of Natural Rubber, Vulcanized with Sulfur and an Accelerator or Bismaleimide and a Peroxide at Different Temperatures

Cure	Sulfur ^a				Bismaleimide ^b			
	Tensile strength, psi	Stress at 300% elongation, psi	Breaking elongation, %	Hardness, Shore A	Tensile strength, psi	Stress at 300% elongation, psi	Breaking elongation, %	Hardness, Shore A
Cure at 300°F., min.								
30	3620	1600	470	58	2920	1450	460	49
60	3410	1425	490	56	3370	1725	470	52
Cure at 350°F., min.								
8	3300	1320	500	56	2990	1725	420	51
16	3016	1075	510	53	2820	1750	390	51
Cure at 400°F., min.								
2	2940	1125	480	52	2730	1639	400	49
4	2280	780	480	48	2600	1690	390	50
Cure at 450°F., min.								
1	1680	600	520	44	1960	1550	330	48
2	1180	485	460	40	2090	1560	370	48
4					1900	1600	340	48

^a Measured on stocks prepared from natural rubber, 40 phr fast-extrusion black, 4 phr pine tar, 3.5 phr sulfur, 1.5 phr stearic acid, 4 phr zinc oxide, and 0.75 phr *N*-cyclohexyl benzothiazole sulfenamide.

^b Measured on stocks prepared from natural rubber, 40 phr fast-extrusion black, 4 phr pine tar, 2.2 phr *N,N'*-*m*-phenylenebismaleimide, and 1 phr dicumyl peroxide, 40% active, on CaCO₃.

TABLE X
Properties of Natural Rubber, Vulcanized with a Bismaleimide and a Monomaleimide at Different Temperatures^a

Cure	Bismaleimide ^b				Monomaleimide ^c			
	Tensile strength, psi	Stress at 300% elongation, psi	Breaking elongation, %	Hardness, Shore A	Tensile strength, psi	Stress at 300% elongation, psi	Breaking elongation, %	Hardness, Shore A
Cure at 300°F., min.								
45	2270	1170	420	49	2000	825	460	48
60	2010	1250	390	50	2150	925	450	49
Cure at 350°F., min.								
8	2120	1300	370	49	2080	850	430	46
16	2160	1325	370	50	1810	875	460	47
Cure at 400°F., min.								
2	2560	1325	410	47	1810	700	460	45
4	2340	1275	400	48	1940	740	450	45
Cure at 450°F., min.								
1	2040	1150	420	46	1420	510	460	43
2	2020	1120	380	45	1250	510	460	40

^a Measured on stocks prepared from natural rubber, 50 phr fast-extrusion black, 6 phr paraffin oil, and 0.75 phr dicumyl peroxide. 40% active, on CaCO₃.

^b Bismaleimide cure accomplished with 1.07 phr of *N,N'*-*m*-phenylenebismaleimide.

^c Monomaleimide cure accomplished with 4.0 phr *N*-phenylmaleimide.

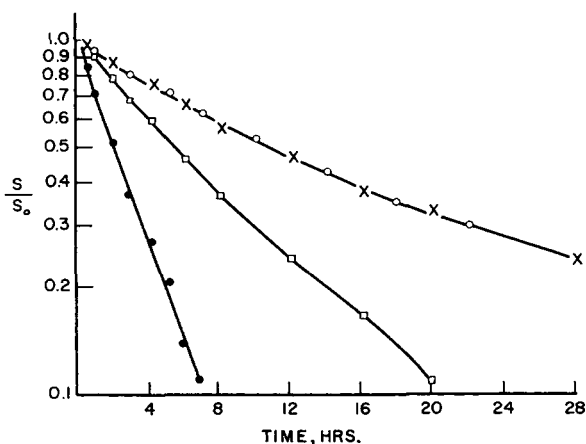


Fig. 1. Effect of curing system on stress relaxation of cured natural rubber stocks. Stress relaxation at 230°F.: (O) Dicup; (X) bismaleimide-Dicup; (□) bismaleimide-MBTS; (●) sulfur.

MBTS or dicumyl peroxide are given in Figure 1. The rates of stress relaxation of the vulcanizates cured with bismaleimide promoted with either dicumyl peroxide or MBTS are lower than the rate of stress relaxation of the sulfur vulcanizate. Therefore, the chains of a sulfur-cured natural rubber sample are more susceptible to oxidation. The resistance to air aging of a sample cured with peroxide-promoted bismaleimide or of a peroxide-cured sample is equal to or better than the resistance to air aging of an MBTS-promoted bismaleimide-cured vulcanizate.

The improved resistance to air aging of bismaleimide-cured SBR is demonstrated in Table XI. A major effect of air aging of a sulfur-cured SBR vulcanizate is the rapidly increasing stress at 300% and at the

TABLE XI
Aging of a Maleimide Cure

Test	Cure	Time aged at 212°F.			
		0 days	2 days	4 days	6 days
Tensile strength, psi	Bismaleimide	2610	1900	1890	1860
	Sulfur	3780	3390	2760	3000
Breaking elongation, %	Bismaleimide	460	370	340	320
	Sulfur	500	330	270	260
300% modulus, psi	Bismaleimide	1225	1360	1400	1375
	Sulfur	1525	2650	(3000) ^a	(3050) ^a
Tear resistance (room temp.), lb./in.	Bismaleimide	4.0	4.6	3.4	3.3
	Sulfur	5.0	1.9	1.6	1.4
Cut growth (150°F.), kcycles/in.	Bismaleimide	7.7	6.3	5.5	10.9
	Sulfur	51.5	11.4	7.8	5.6

^a Extrapolated.

same time decreasing breaking elongation, tear resistance, and cut growth resistance. These effects are much less pronounced in a bismaleimide-cured SBR vulcanizate.

Low Temperature Properties of Maleimide Vulcanizates

For sulfur-cured natural rubber the low temperature retraction test (ASTM D 599-55 and D 1329-58T) is used as a quantitative method to determine the state of cure and as a method for rapid evaluation of crystallization effects. A stretched sample is cooled to -70°C . and then gradually warmed up. The temperature at which the test piece has retracted to 50% of the applied elongation (T_{50}) is used to characterize the state of cure of the sample. This test has extensive application for checking cures in production.

In Figures 2 and 3 are given the retraction curves for natural rubber stocks cured with sulfur (100 parts natural rubber, 40 phr fast-extrusion black, 2 phr zinc oxide, 3 phr stearic acid, 0.5 phr *N*-cyclohexyl benzothiazole sulfenamide, and 2.5 phr sulfur) and with a bismaleimide (100 parts natural rubber, 40 phr fast extrusion black, 1.5 phr *N,N'*-*m*-phenylenebismaleimide, and 1.25 phr dicumyl peroxide, 40% active, on CaCO_3).

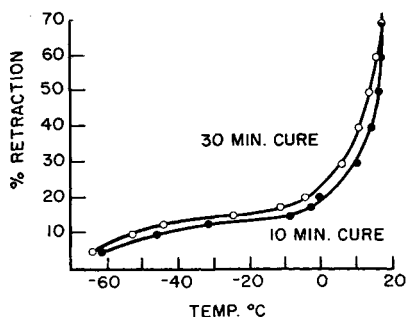


Fig. 2. Low-temperature retraction of natural rubber cured at 307°F . with either sulfur or a bismaleimide.

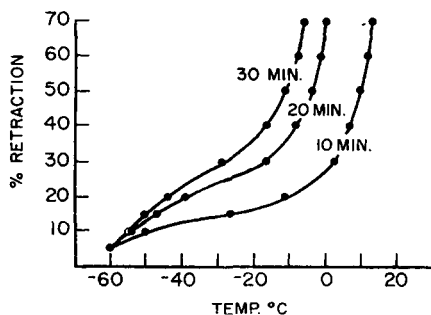


Fig. 3. Low temperature retraction of sulfur-cured natural rubber stocks at 292°F .

The T_{50} value of a sulfur-cured sample decreases with increasing cure time. However, the T_{50} value of the bismaleimide-cured sample decreases only very slightly under similar conditions. In Figure 4 the T_{50} values of both samples are plotted against the stress at 300% elongation. The T_{50} value of the sulfur-cured sample shows a good correlation with the state of cure, expressed as stress at 300%. No such correlation is found for the maleimide-cured samples. Although the state of cure of these samples covers a wide range, the T_{50} values vary only slightly.

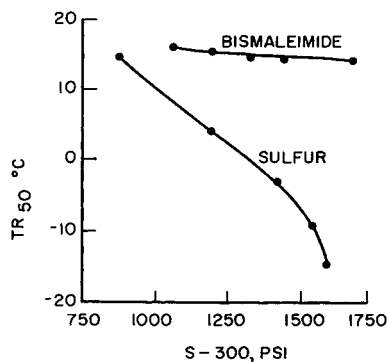


Fig. 4. Plot of low temperature retraction vs. stress at 300% elongation for natural rubber cured with either sulfur or a bismaleimide.

The difference between the temperature at which a vulcanizate retracts 10% (TR_{10}) and the temperature at which a vulcanizate retracts 70% (TR_{70}) increases as the tendency to crystallize increases. In Table XII the TR_{10} - TR_{70} values of a sulfur-cured natural rubber sample decreases with increasing cure time, indicating a reduction of the tendency of natural rubber to crystallize during the progress of the cure. This is not observed for a monomaleimide- or bismaleimide-cured natural rubber sample.

TABLE XII

$TR_{70} - TR_{10}$ as a Measure of the Tendency to Crystallize in Various Vulcanizates

Curing system	Cure temp., °F	$TR_{70} - TR_{10}$, °C., for various cure times				
		10	15	20	25	30
		min.	min.	min.	min.	min.
Sulfur + <i>N</i> -cyclohexyl benzothiazole sulfenamide	293	63	60	55	50	50
<i>N,N'</i> - <i>m</i> -Phenylenbismaleimide + dicumyl peroxide	307	64	67	67	68	69
<i>N</i> -Phenylmaleimide + dicumyl peroxide	307	66	65	65	65	66
Dicumyl peroxide	307	68	67	67	62	66
<i>N,N'</i> - <i>m</i> -Phenylenbismaleimide + MBTS	331	65	64	64	64	64
<i>N</i> -Phenylmaleimide + MBTS	331	64	64	64	64	64

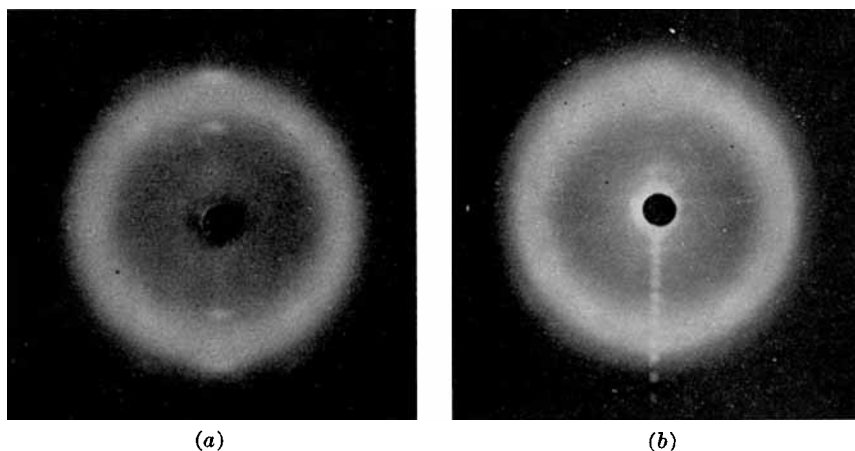


Fig. 5. X-ray diffraction patterns: (a) natural rubber cured with a bismaleimide recipe and stretched 300%; (b) natural rubber cured with a sulfur recipe and stretched 300%.

The x-ray diffraction patterns of stretched samples of sulfur and bismaleimide cured natural rubber (Fig. 5) confirm the results based on the low temperature retraction experiments. At 300% elongation, a gum sample of bismaleimide-cured natural rubber shows the first indication of crystallization, while the sulfur sample is still amorphous at the same elongation.

The small decrease of the T_{50} values of the bismaleimide vulcanizates over a curing time range can be attributed to the increasing amount of crosslinks. A crosslink restricts the free movement of the polymer chain and therefore reduces the chance for this polymer chain to crystallize. However, the large decrease of the T_{50} values of the sulfur vulcanizates must be attributed to chemical modifications of the polymer other than the crosslinking reaction. Two possible side reactions during the sulfur vulcanization are *cis-trans* isomerization of the natural rubber or the formation of cyclic sulfides in the polymer chain. Infrared spectra of sulfur- and dicumyl peroxide-cured natural rubber differ only in the appearance of an absorption band at 10.4μ in the spectrum of sulfur cured natural rubber. Bands used to determine a *cis-trans* isomerization of natural rubber were the same for both samples. Shipman and Golub¹¹ have recently demonstrated that the 10.4μ band of sulfur-vulcanized natural rubber arises largely from a combination of saturated ring structures, such as cyclic sulfides and conjugated double bonds, and to a minor extent from shifted double bonds as proposed by Sheppard and Sutherland.¹² Therefore, it is most likely that the formation of these cyclic sulfides reduces the tendency of sulfur-cured natural rubber to crystallize on stretching. Heinze¹³ reported that sulfur vulcanization results in a much greater temperature displacement of the second-order transition point of natural rubber than does peroxide or high energy radiation vulcanization at the same crosslink density. The intramolecular addition of sulfur is predominantly responsible for the increased temperature displacement.

A qualitative measurement of the second-order transition point of natural rubber is the T_{10} value obtained in the Gehman low temperature torsional modulus test (ASTM D 1053-58T). This is the temperature at which a vulcanizate attains a relative modulus of ten times the modulus at room temperature. In Table XIII the T_{10} values of an accelerated sulfur- and a maleimide-cured sample are given.

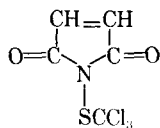
TABLE XIII
 T_{10} Values for Sulfur and Maleimide Cures

Cure	Cure temp., °C.	Cure time, min.	T_{10} , °C.
Sulfur	292	10	-54
	292	30	-52
Bismaleimide	307	10	-56
	307	30	-56

The T_{10} value of an accelerated sulfur-cured sample is higher than the T_{10} value of a bismaleimide-cured sample, perhaps due to the plasticization effect of the stearic acid. The small increase in T_{10} value with increased cure time might be due to the stiffening effect of the intramolecular cyclic sulfides.

Multipurpose Maleimides

Maleimides which serve not only as curing agents but which simultaneously have other uses have been obtained by substituting a suitable functional group on the nitrogen of maleimide. *N*-Trichloromethylthiomaleimide (VIII) contains the N-S bond characteristic of a sulfenamide acceler-



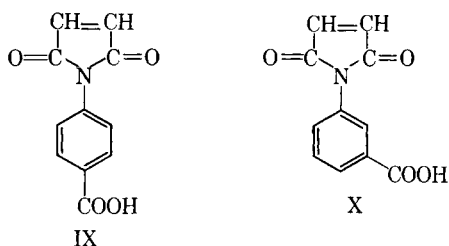
VIII

TABLE XIV
N-Trichloromethylmaleimide as Accelerator and Curing Agent

Composition, parts				
SBR 1500	100	100		
Smoked Sheet			100	100
Philblack O	50	50	50	50
<i>N</i> -Trichloromethylmaleimide	3.7		4.3	
<i>N</i> -Phenylmaleimide		2.6		3.0
Cured 30 min. at 330°F.				
Properties				
Tensile strength, psi	1860	256	1340	400
Breaking elongation, %	380	880	430	750
Stress at 300% elongation, psi	1160	115	680	75

ator. The data of Table XIV show that compound VIII alone gives good cures of SBR or natural rubber. In contrast, an equivalent amount of *N*-phenylmaleimide, which contains no accelerating functional group, produces only slight cures under the same conditions.

Powerful promoters of rubber-to-metal adhesion result when a carboxylic acid group is introduced on the aromatic ring of *N*-phenylmaleimide, as in *N*-(4-carboxyphenyl)maleimide (IX) or its *meta* isomer (X). Table XV

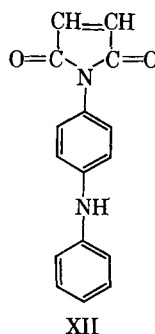
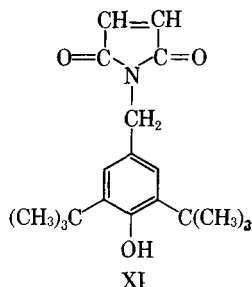


shows that compounds IX and X produce strong rubber-to-metal bonding. Apparently the carboxylic acid groups form ionic bonds between the metal and the rubber chains, for when the maleimide and carboxylic acid functions are separated into two molecules (*N*-phenylmaleimide + benzoic acid) almost no rubber-to-metal adhesion occurs. Similar results were obtained for the adhesion of polyurethane and ethylene-propylene rubbers to metals.

TABLE XV
Maleimides as Rubber-to-Metal Adhesives

Composition, parts				
SBR 1500	100	100	100	100
Fast extrusion black	50	50	50	50
Paraffin oil	7.5	7.5	7.5	7.5
<i>N</i> -(4-Carboxyphenyl)maleimide	5.0			
<i>N</i> -(3-Carboxyphenyl)maleimide		4.0		
<i>m</i> -Phenylenebis(maleamic acid)			1.5	
<i>N</i> -Phenylmaleimide				4.0
Benzoic acid				2.8
Dicumyl peroxide, 40% active, on CaCO ₃ (Hercules Powder Co.)	0.7	0.7	0.7	0.7
Cured 45 min. at 320°F.				
Properties				
Tensile strength, psi	2915	2250	2230	3060
Breaking elongation, %	530	580	420	520
Stress at 300% elongation, psi	1075	810	1100	1180
Adhesion to hot-rolled steel, psi	2225	1720	1620	85

The compounds XI and XII were prepared in attempts to incorporate antioxidant or antiozonant functions into maleimide derivatives. However, these compounds prevented vulcanization with either MBTS or dicu-



myl peroxide initiation, probably by capture of the free radicals which would have initiated crosslinking.

We thank Dr. Elbert C. Ladd and Mr. Merlin P. Harvey for their syntheses of the maleimides examined in this work.

References

1. Tawney, P. O., R. H. Snyder, C. E. Bryan, R. P. Conger, F. S. Dovell, R. J. Kelly, and C. H. Stiteler, *J. Org. Chem.*, **25**, 56 (1960).
2. Tawney, P. O., R. H. Snyder, R. P. Conger, K. A. Leibbrand, C. H. Stiteler, and A. R. Williams, *J. Org. Chem.*, **26**, 15 (1961).
3. Kovacic, P., and R. W. Hein, *J. Am. Chem. Soc.*, **81**, 1187, 1190 (1959); *Rubber Chem. Technol.*, **35**, 520, 528 (1962).
4. Goldberg, E. J., U. S. Pat. 2,925,407 (Feb. 16, 1960).
5. Goldberg, E. J., U. S. Pat. 2,958,672 (Nov. 1, 1960).
6. Dixon, S., and E. J. Goldberg, U. S. Pat. 2,965,553 (Dec. 20, 1960).
7. Little, J. R., U. S. Pat. 2,989,504 (June 20, 1961).
8. Juve, A. E., and B. S. Garvey, *Ind. Eng. Chem.*, **36**, 212 (1944).
9. Svetlik, J. F., and H. E. Railsback, *Rubber Age (N. Y.)*, **78**, 889 (1956).
10. Smith, F. B., *Proc. Intern. Rubber Conf., Washington, D. C. 1959*, p. 604; *Rubber Chem. Technol.*, **34**, 571 (1961).
11. Shipman, J. J., and M. A. Golub, *J. Polymer Sci.*, **58**, 1063 (1962).
12. Sheppard, N., and G. B. M. Sutherland, *J. Chem. Soc.*, **1947**, 1699; *Rubber Chem. Technol.*, **21**, 799 (1948).
13. Heinze, H. D., K. Schmieder, G. Schnell, and K. A. Wolf, *Rubber Chem. Technol.*, **35**, 776 (1962).

Résumé

On a testé des séries de mono- et bis-maléimides comme agents de vulcanisation pour déterminer l'effet de la structure sur les possibilités de pontage. L'activité des dérivés de la *N*-phénylmaléimide (monomaléimide) comme agents de pontage dépend fortement du substituant du groupe phényle. L'activité des bismaléimides est semblablement influencée par la nature de la partie qui unit les noyaux maléimides. Les isomaléimides et les itaconimides sont des agents moins efficaces. Les initiateurs pour les vulcanisations avec le maléimide comprennent des peroxydes et des accélérateurs à base de soufre du type thiazole. Les caoutchoucs d'hydrocarbures saturés ou non, sauf ceux qui contiennent un haut pourcentage d'unités isobutylène, sont vulcanisés par un système à initiateur maléimide. L'attrait du système de vulcanisation à la maléimide est du au fait que les propriétés physiques des caoutchoucs traités sont indépendantes de la température du traitement. De plus ces produits vulcanisés ont de bonnes caractéristiques de vieillisse-

ment typiques des produits vulcanisés par un agent traitant non-sulfuré. Par contraste avec la vulcanisation au soufre, les systèmes de vulcanisation à la maléimide n'affectent pas de façon marquante l'aptitude des élastomères à cristalliser lorsqu'on les étire. Dès lors le test T_{50} ne peut être utilisé pour établir l'état de vulcanisation des maléimides-caoutchouc naturel. Les maléimides contenant un groupe fonctionnel approprié peuvent être utilisés comme agent de vulcanisation auto-accélérateur ou adhésif.

Zusammenfassung

Reihen von Mono- und Bismaleinimiden wurden in bezug auf ihre Fähigkeit als Vulkanisationsmittel untersucht, um den Einfluss der Struktur auf die Vernetzungswirkung zu bestimmen. Die Aktivität von *N*-Phenylmaleinimidderivaten (Monomaleinimiden) als Vernetzungsmittel hängt in hohem Grade vom Substituenten an der Phenylgruppe ab. Die Aktivität von Bismaleinimiden wird in gleicher Weise durch die Natur des die Maleinimidringe verbindenden Teiles beeinflusst. Isomaleinimide und Itaconimide sind als Vulkanisationsmittel weniger wirksam. Als Starter für die Maleinimidvulkanisation können Peroxyde und Schwefelbeschleuniger vom Thiazoltyp verwendet werden. Kautschuke vom gesättigten und ungesättigten Kohlenwasserstofftyp, ausgenommen solche mit einem hohen Prozentsatz an Isobutyleneinheiten, können mit einem Maleinimid-Startersystem vulkanisiert werden. Eine der reizvollen Eigenschaften eines Maleinimid-Vulkanisationssystems ist die Unabhängigkeit der physikalischen Eigenschaften des vulkanisierten Kautschuks von der Vulkanisationstemperatur. Weiters besitzen diese Vulkanisate die gute, für schwefelfrei vulkanisierte Produkte typische Alterungscharakteristik. Im Gegensatz zur Schwefelvulkanisation beeinflussen die Maleinimidvulkanisationssysteme die Kristallisationsfähigkeit der Elastomeren bei der Dehnung nicht merklich. Daher kann der " T_{50} Test" nicht zur Beurteilung des Vulkanisationsgrades von Maleinimid-Naturkautschukvulkanisaten verwendet werden. Maleinimide mit einer zweiten geeigneten Funktionellen Gruppe können als selbstbeschleunigende Vulkanisationsmittel oder als Klebstoffe verwendet werden.

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