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Future Trends in Rubber Processing: The Chemistry of Rubber Processing

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FUTURE TRENDS IN RUBBER PROCESSING: THE CHEMISTRY OF RUBBER PROCESSING

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ABSTRACT

Future trends in rubber processing are discussed with special emphasis on the chemical aspects that might be used to develop new and improved properties of rubber materials. They include optimization of such properties as resiliency and "softness," of reinforcement and the control of crosslinking, and of the crosslink densities of rubbers during vulcanization.

INTRODUCTION

The rubber industry faces many challenges in optimizing the properties of rubber materials and rubber goods. This is not only desired for the optimization of specific and ultimate properties, but also for the problems of producing these materials effectively and cost efficiently.

The following demands are major requirements:

(1). To improve the quality of rubber materials for high performance
(2). To achieve specialized functional properties
(3). To lower production costs
(4). To establish economical methods for recycle/reuse of rubber scraps without pollution
(5). To preserve the environment in the workplace.

In this article I am specifically discussing Point (1): Rubber processing from the chemical point of view for quality improvement to produce high performance rubber materials. In my opinion, the introduction of relatively simple but well-established and cost-effective chemical reactions involving commercially used chemicals other than the vulcanization reaction would seem to be the most effectual means to produce elastomeric materials, rubber goods, of high performance value.

Several essential properties are required for rubber materials and rubber goods in producing the final products for customer uses. They include "rubber behavior," which includes softness, resiliency, and strength. Sometimes the strength factor is the major and determining characteristic of rubber materials.

Softness as the determining property in a rubber has been the focus of much research and has been fine-tuned for the perspective application.

SOFT ELASTOMERS OF HIGH RESILIENCY

It is not always easy to combine good processability of rubber materials and maximum mechanical properties of the rubber vulcanizate in a practical way. In fact, very often they are not always produced together and consistently. This problem can be overcome by using some additives like reactive oligomers which react readily with the elastomeric macromolecules of the rubber materials. Examples of such suitable regents are: (a) 1-chlorobutadiene-1,3-butadiene-1,3 rubber; (b) digycidylethers of Bisphenol A; and (c) hydroxy-terminated liquid rubber—with reactive "softeners."

1-Chlorobutadiene-Butadiene Rubber (CB-BR)

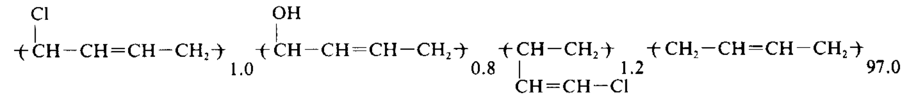
1-Chlorobutadiene-1,3 is a by-product of the preparation of 2-chlorobutadiene-1,3. It is obtained by chlorination of butadiene-1,3 followed by dehydrochlorination. It is presumably the consequence of dehydrochlorination of 1,2-dichlorobutene-3,4. A molecule of hydrogen chloride can remove either the chlorine of the 2-position rather than the desired dehydrochlorination, the chlorine atom from the 1-position. 1-Chlorobutadiene-1,3 is copolymerizable with butadiene-1,3. Emulsion copolymerization gave the novel 1-chlorobutadiene-1,3/butadiene-1,3 copolymer rubber (CB-BR) with hydroxyl groups and reactive chlorine atoms attached to the 1,4-units [1, 2] (Table 1). The hydroxyl groups undoubtedly form during emulsion polymerization as end groups and also probably by inadvertent hydrolysis of the labile chlorine atoms $-CH_2CHC-CH=-CH-$ of the chlorobutadiene units. These functional groups suggest the possibilities of various chemical modification reactions of the $-OH$ and $-Cl$ groups and nonsulfur vulcanization based on the $-CHCl-$unit [3].

Diglycidylether of Bisphenol A as Reactant for Softer Rubbers

The diglycidylether of Bisphenol A (DGEBA) can provide softening characteristics to rubbers and is used as both a "softener" and as a curing agent. The curing reaction is carried out in the presence of anhydrides; its mechanism is shown in Scheme 1.

The epoxy resin formed in the rubber matrix after curing acts as a reinforcing filler. Figure 1 shows the effect of the "softener" on the modulus. The modulus at

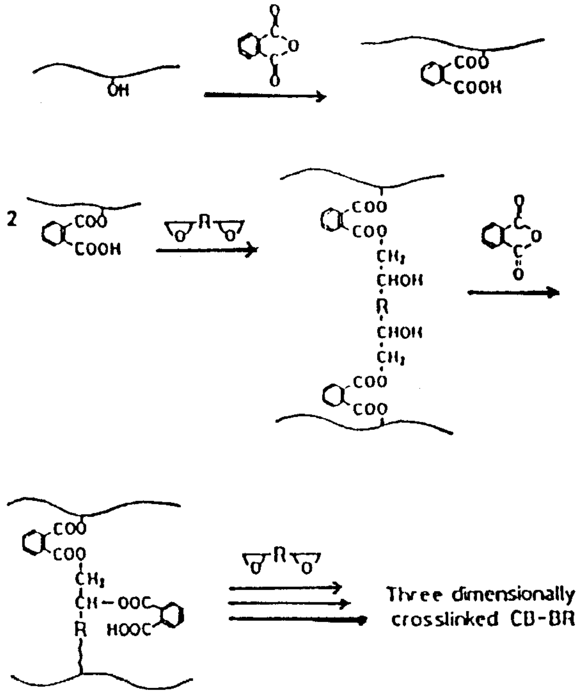
TABLE 1. Structure and Properties of 1-Chlorobutadiene-Butadiene Rubber [1]



$$-\!(\overset{\mathrm{Cl}}{\mathrm{C}}\mathrm{H}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2})_{1.0}\!-\;-\!(\overset{\mathrm{OH}}{\mathrm{C}}\mathrm{H}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2})_{0.8}\!-\;-\!(\underset{\mathrm{CH=CH-Cl}}{\mathrm{CH}}-\mathrm{CH_2})_{1.2}\!-\;-\!(\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2})_{97.0}\!-$$

Properties	
$[\eta]^a$	2.75
M_n	8.8×10^4
M_η	53.8×10^4
Cl (10^4 mol/g)[b]	4.0
OH (10^4 mol/g)[c]	1.4

[a] Toluene at 25.9°C.
[b] Elemental analysis.
[c] UV method.



SCHEME 1. Crosslinking of 1-chlorobutadiene-butadiene-butadiene rubber by diglycidylether of Bisphenol A and acid anhydride.

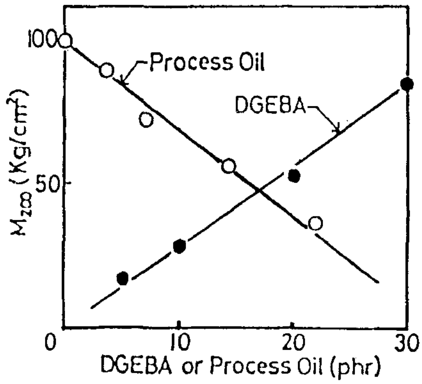


FIG. 1. Effect of softeners on M_{200} of 1-chlorobutadiene-butadiene rubber vulcanizates [3].

200% elongation (M_{200}) of the vulcanizate of the compounded mixture that was made in the presence of DGEBA increased with the amount of DGEBA. Usually "softeners," i.e., processing oils, lower the modulus of the vulcanizate as shown in Fig. 1.

Hydroxyl-Terminated Liquid Rubber as a Reactive Softening Agent

Hydroxyl-terminated liquid rubber, specifically hydroxyl-terminated liquid butadiene-1,3 rubber (HT-BR) has also been found to act as a reactive softener for CB-BR [3]. HT-BR is first compounded with CB-BR and the compound is then cured with diisocyanate. Figure 2 shows the Mooney viscosity of CB-BR stocks compounded with various amounts of HT-BR. It also demonstrates that the Mooney viscosity decreases dramatically with increasing amounts of HT-BR in the compounded mixture. (See also Fig. 3.)

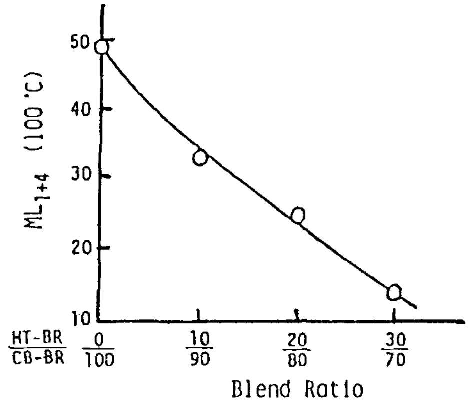


FIG. 2. Effect of hydroxy-terminated liquid butadiene rubber on the Mooney viscosity of 1-chlorobutadiene-butadiene rubber compounds [3].

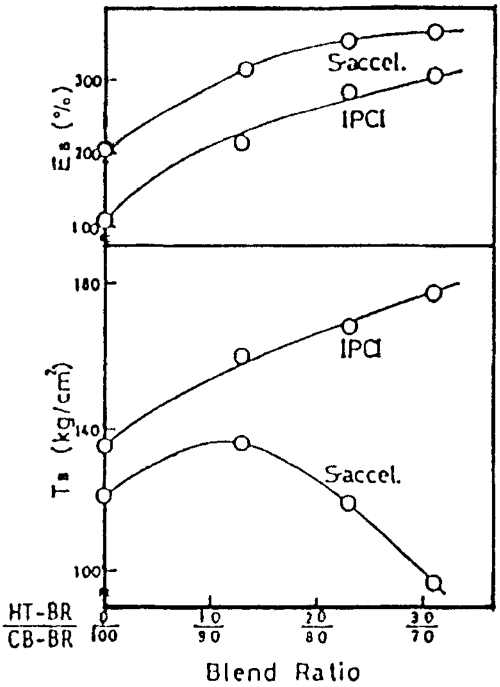


FIG. 3. Effect of hydroxy-terminated liquid butadiene rubber blending on the tensile properties of carbon-black-loaded 1-chlorobutadiene-butadiene rubber vulcanizates [3].

REINFORCEMENT OF RUBBER MATERIALS

The mechanical properties of elastomers can be improved by the use of fillers which co-react with the base elastomer during compounding and vulcanization. Efficient interaction between the rubber and the "reactive" filler surface produces the optimal properties of vulcanized rubber materials and must be taken into account during the design. The most commonly used fillers for rubber materials are (a) carbon black, (b) silica, (c) calcium carbonate, and (d) lignin.

Carbon Black

Reinforcement of rubber materials is the most important reinforcement at the present time for rubber tires. There are two important requirements for passenger car tire treads: 1) to reduce the rolling resistance to reduce fuel consumption, and 2) to improve wet skid resistance for safety. In order to influence the viscoelastic properties of the target polymers, it was found that polymer possesses lower tan δ at 50–70°C, which is relevant to the rolling resistance; a higher tan δ, at about 0°C, influences the wet skid resistance (Fig. 4) [4].

Monochelic Styrene-Butadiene Rubber

Sn-Coupled Styrene-Butadiene Rubber. A new polymerized styrene-butadiene rubber (SBR) has Sn—C bonds, especially Sn—butadienyl bonds, at the ends of the polymer chains, as shown in Scheme 2 [5]. Sn-coupled SBR was found

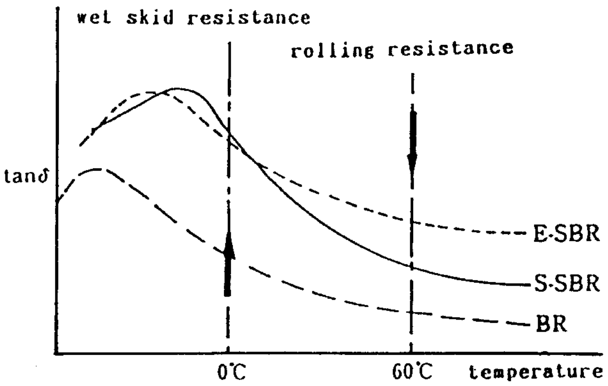
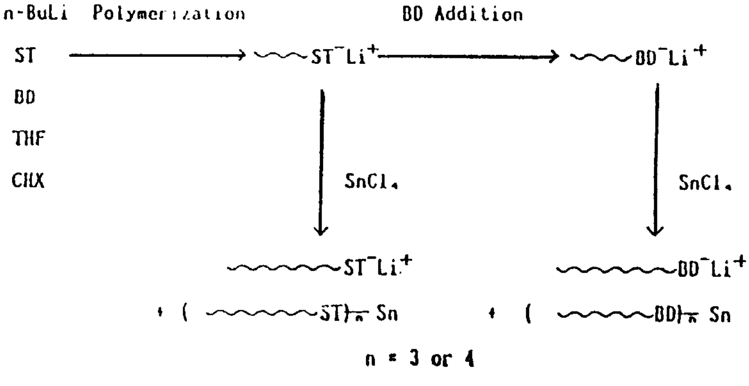


FIG. 4. Temperature dispersion of tan δ.

to impart a significant improvement to the rolling resistance of the SBR without sacrificing its mechanical properties (Fig. 5). This improvement is caused by the chemical interaction between the polymer chain ends and the surface of the carbon black, and it improves the carbon black dispersion.

Figure 6 shows the difference in the reactivity of polybutadiene with Sn-bonds with model compounds. Only quinone-type compounds among the model compounds with carbonyl groups were also similarly reactive. It is suggested that SBR with Sn—butadienyl bonds at the polymer ends can more readily react with quinone groups that exist on the carbon black surfaces and form polymer—carbon black bonds.

Styrene-Butadiene Rubber Reaction Product with 4,4′-Bis(diethylamino)-benzophenone. Another chemically modified SBR was prepared by synthesizing SBR in solution by anionic polymerization using *n*-butyllithium as the initiator and then terminating the living polymerization with 4,4′-bis(diethylamino)-benzophenone (EAB) (Scheme 3) [6].



SCHEME 2. Polymerization and coupling reaction schemes [5].

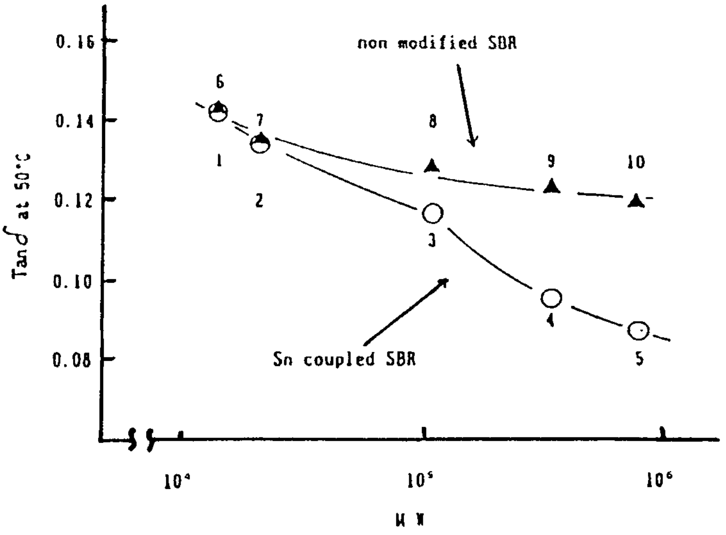


FIG. 5. Effect of molecular weight of Sn-coupled styrene-butadiene rubber on tan δ: (○) blend of nonmodified and Sn-coupled styrene-butadiene rubber, (▲) blend of nonmodified styrene-butadiene rubber and nonmodified styrene-butadiene rubbers of various molecular weights [6].

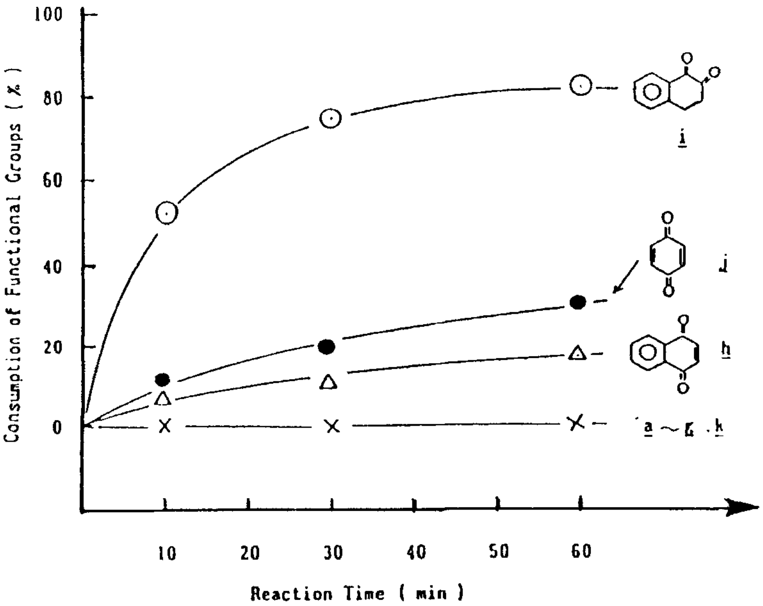
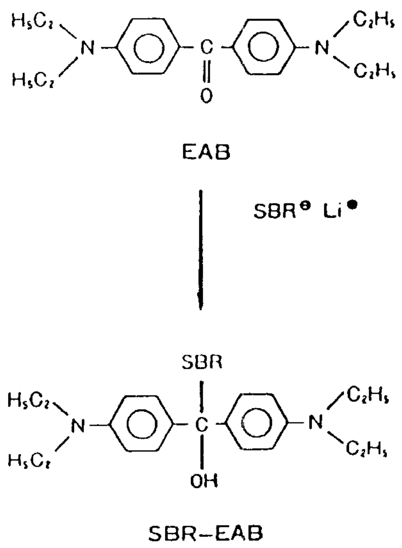


FIG. 6. Difference in reactivity of model compounds with polybutadiene modified with tri-*n*-butyltin chloride [5].



SCHEME 3. From Reference 6.

Figure 7 shows the temperature dependence of the rebound resiliences for common SBR prepared in solution (S-SBR) and EAB-terminated SBR. The relevant compounds are described in Table 2.

N,N′-Bis(2-methyl-1,2-nitropropyl)-1,6-diaminohexane as Coupling Agent

N,N′-Bis(2-methyl-1,2-nitropropyl)-1,6-diaminohexane (BNAH) was developed as a new nonnitroso type coupling agent [7] to increase the interaction of SBR and carbon black. Several properties were improved when BNAH was added to the SBR/carbon black compound. They include such dynamic properties as resilience, heat build-up, and tan δ (Tables 3 and 4). A possible mechanism describing the coupling reaction shown in Scheme 4 is based on two pathways from the results of various spectroscopic analyses [8].

From Fig. 7 it can be seen that when EAB is attached to the end of SBR chains, these molecules contribute to the increase of the rebound resiliency. For the dry-mixed compound, as shown in Fig. 8, the modulus of compound B at relatively large elongations, such as 100% or more, is about twice as high as that of compound A.

It can be concluded that the EAB reaction product and the SnO-coupled SBRs are interesting from the point of view of the reaction of the interface between the rubber polymer chain and the carbon black surface.

Silica

Silica is the most important and widely used reinforcing filler in the rubber industry. Compared to carbon black, which is widely used in its various forms and with different surface properties, the use of silica as a reinforcement agent produces filled rubbers with limited materials properties. The inevitable faults are large compression sets, low abrasion resistance, and high heat build-up. These properties

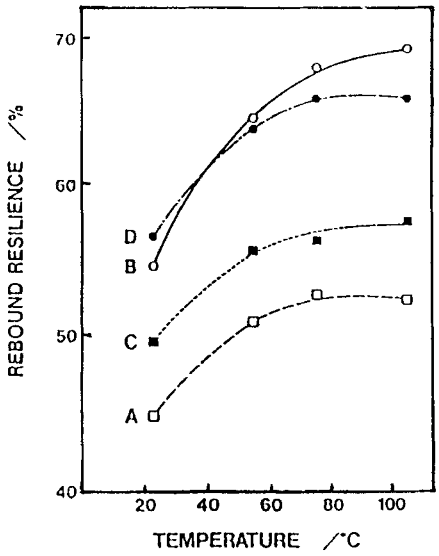


FIG. 7. Temperature dependence of rebound resiliences of the dry mixed compounds A, B, C, and D [6].

are developed by silica structures formed during the vulcanization process. Many approaches have been undertaken to overcome these problems and to optimize the properties of silica-filled rubber. They include the use of suitable silane coupling agents, the use of bis(diisopropylthiophosphoryl)disulfide, and the use of epoxidized diene rubber.

Silanes as Coupling Agents

Silane coupling agents are used to introduce functional groups onto silica particles as well as to improve their dispersion into the rubber matrix. A proposed reaction scheme is indicated in Scheme 5. In Table 5 [9] the properties of silica-

TABLE 2. Compound Used for the Testing of the Physical Properties of Vulcanizates [6]

Compound	A	B	C	D
S-SBR	100	–	100	–
SBR-EAB	–	100	–	100
CB-N (N330)	50	50	–	–
CB-S[a]	–	–	50	50
Dicumyl peroxide	1	1	1	1

[a]Carbon black (N330) surface treated with saturated adsorption of *n*-butyl-EAB.

TABLE 3. Formulation of Compounds [7]

	Parts by weight
NR (RSS 1)	100
N330 black	45
Silica	10
Stearic acid	3
Zinc oxide	5
Vulcanization accelerator (*N*-cyclohexyl-2-benzothiazol sulfonamide)	1
Sulfur	2
BNAH	Variable

loaded SBR are shown with special emphasis on the treatment of silica with mercaptosilane. The best mechanical properties of the vulcanizate were obtained when silica that had been treated with mercaptosilane, Silane A-189, was used.

Bis(triethoxysilylpropyl)tetrasulfide (TESPT), Si-69, is also a good and useful silane coupling agent. A special mixing procedure for a recipe of TESPT with EPDM has been described by Cochet et al. [10].

Bis(diisopropylthiophosphoryl)disulfide, $(C_2H_5O-)_3-Si-(-CH_2)_3-S-S-S-S-(CH_2)_3-Si-(OC_2H_5)3$, as Coupling Agent

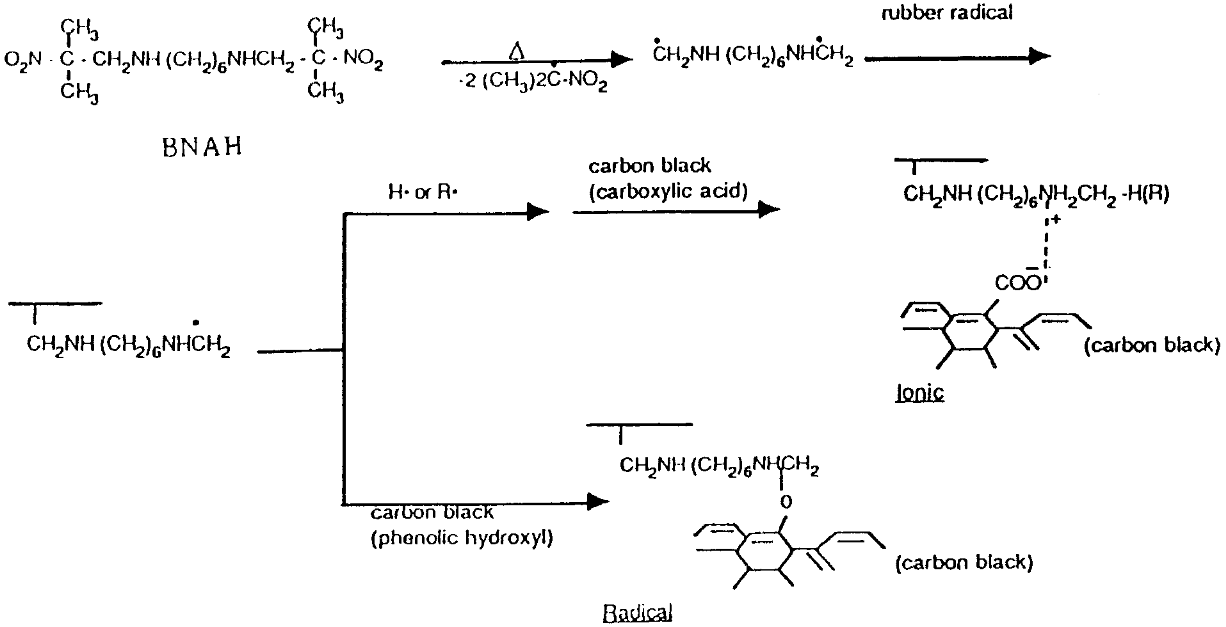
Bis(diisopropylthiophosphoryl)disulfide (DIPDIS) acts as a powerful coupling agent for facilitating the interaction of silica with diene rubber, although the mechanism of interaction differs from that of the silane coupling agent on silica and diene rubber. DIPS is believed to react and interact not only with the silica surface but it also reacts with the diene rubber as indicated in Scheme 6 [11].

Epoxidized Natural Rubber

Epoxidized natural rubber (ENR) [12] exhibits a unique feature when used in combination with silica as the filler. It shows a reinforcement of the diene rubber equivalent to the effectiveness of carbon black as the reinforcement filler, even

TABLE 4. Performance of Rubbers in a System Loaded with Carbon Black and Silica [7]

	Tensile property						
BNAH, phr[a]	TS, MPa	EB, %	M_{100}, MPa	M_{300}, MPa	Resilience, %	Heat build-up ΔT, °C	Tan δ at 60°C
0	26.5	460	3.4	11.5	59	49	0.122
1	28.2	470	3.8	17.5	62	42	0.095
2	27.8	460	3.9	17.8	63	39	0.089
3	27.3	450	4.0	18.1	63	39	0.074



SCHEME 4. Possible reaction mechanism [8].

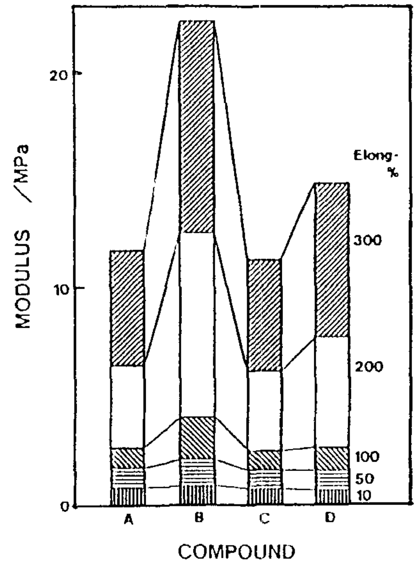


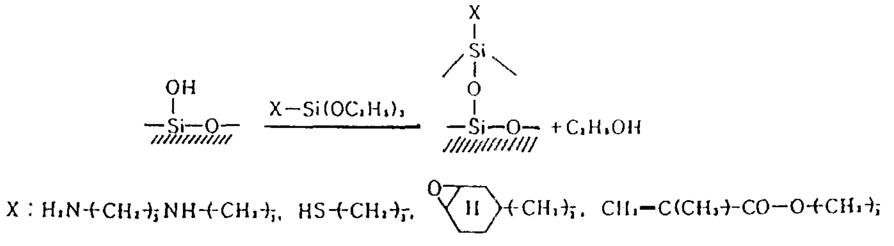
FIG. 8. Moduli at various elongations of the dry mixed compounds as indicated [6].

though ENR was used without the use of additional coupling agent as shown in Table 6.

The epoxy groups of the ENR seem to react with the surface (possibly —OH groups) of the silica and bind the ENR permanently to the silicia surface. As a consequence, the ENR-silica-filled compositions have the potential of providing white and colored vulcanizates with the properties of carbon-black-filled compounds.

Calcium Carbonate

Calcium is a very attractive filler for rubber compounds. It is inexpensive, white, and readily available. The reinforcing ability of calcium carbonate, however, as it is now available, is relatively low because it has a rather inactive surface. Efforts have been made to increase the activated calcium carbonate surfaces. One approach was to introduce carbon dioxide gas into aqueous solutions or suspensions



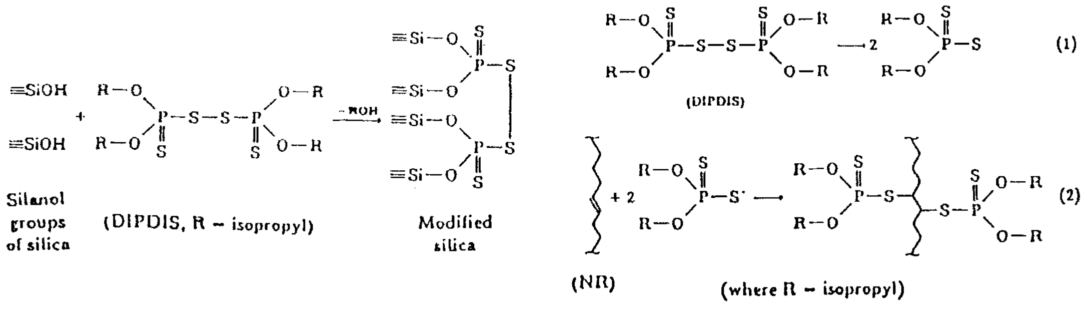
SCHEME 5.

TABLE 5. Use of Mercaptosilane in HS-200 Silica-Loaded Styrene-Butadiene Rubber [9]

Formulation:		
SBR 1502	100	100
Hi-Sil 210	60	60
Silane A-189	–	1.2
Aromatic oil	10	10
Stearic acid	1	1
PBNA	1	1
Santocure NS	1.5	1.2
DOTG	1.5	1.2
TMTD	0.2	–
Sulfur	2.5	2.5
ZnO	4.0	4.0
Properties:		
Mooney scorch at 132°C, T_5, minutes	>30	>30
Optimum cure, minutes at 149°C	30	39
Stress at 300%, MPa	4.7	12.0
Tensile strength, MPa	20.0	23.4
Elongation, %	640	450
Hardness, Shore A	72	66
Goodrich heat build-up, °C	46	28
Pico abrasion index, %	71	119

of calcium hydroxide containing a coupling agent. Generally these agents have two functional groups: one group is reactive and interacts with the calcium carbonate formed during the preparation, and the second function is tailored to interact with the rubber molecule or during vulcanization (Fig. 9).

Several types of coupling agents, such as sorbic acid, *p*-azidobenzoic acid, and various phosphate derivatives, have been reported.



Reaction of silica with DIPDIS.

The reaction of DIPDIS and rubber hydrocarbon

SCHEME 6. From Reference 11.

TABLE 6. Comparison of Carbon-Black-Filled and Silica-Filled Vulcanizates [12]

	NR		ENR-25	
	Black	Silica	Black	Silica
Rubber	100	100	100	100
Sodium carbonate			0.3	0.3
Black (N330)	50		50	
Silica (Hi-Sil 233)		50		50
Process oil	4	4	4	4
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Antioxidant	2	2	2	2
Sulfur	2	2	2	2
MBS	1.5	1.5	1.5	1.5
DPG		0.5		0.5
Hardness, IRHD	65	69	69	67
Modulus at 300%, MPa	11.9	5.8	12.4	12.8
Tensile strength, MPa	29.4	23.2	25.4	21.0
Elongation-at-break, %	495	720	435	405
Akron abrasion, mm^3/500 rev	21	63	14	15
DIN abrasion, mm^3	199	364	272	250
Compression set, 25% 24 h/70°C, %	18	32	17	18
Ring fatigue, 0–100%, kcs	70	51	65	52
Goodrich HBU, 30 minutes at 100°C, ΔT, °C	7	47	7	7

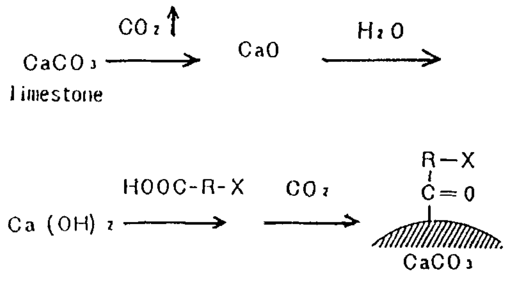


FIG. 9. Schematic illustration of reactive calcium carbonate production [13].

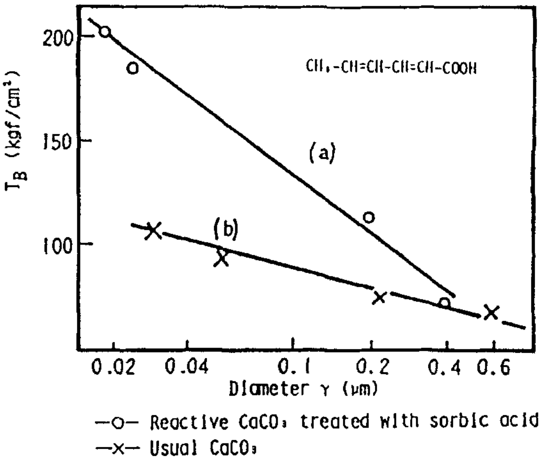


FIG. 10. Comparison of the effects of reinforcement of reactive calcium carbonate with those of regular calcium carbonate [13]. Loading, 100 phr; amount of sorbic acid used, 6 g/100 CaO.

Sorbic Acid

Sorbic-acid-activated calcium carbonate has been found to be a very attractive and effective filler for diene rubber vulcanizates. It gives rubber samples with extremely high tensile strengths (Figs. 10 and 11) and good mechanical properties (Fig. 12). These results are an excellent indication of the important role that a relatively inactive filler can play in increasing the reinforcing capability of the rubber when the surface of the filler is appropriately modified.

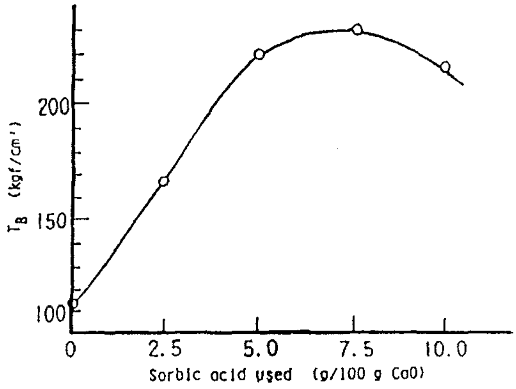


FIG. 11. Effect of reinforcement of reactive calcium carbonate, treated with sorbic acid [13]. Recipe: NBR 100, ZnO 5, Stearic acid 1, S 2, DM 1.5, TMTD 0.2, active $CaCO_3$ 100.

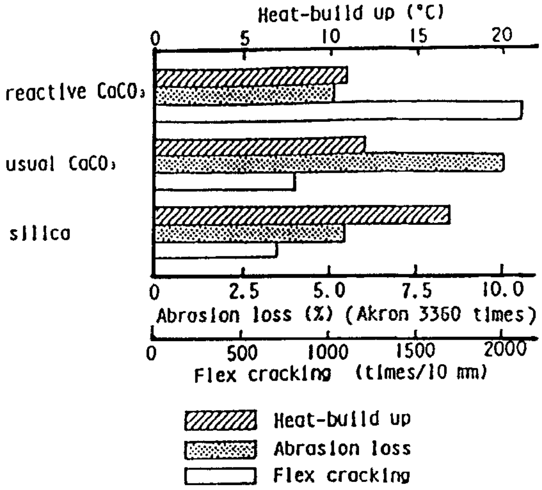


FIG. 12. Results of some mechanical tests of natural rubber vulcanizates loaded with white filler 2 [13].

p-Azidobenzoic Acid

It was found that "ultrafine" calcium carbonate can be modified with *p*-azidobenzoic acid, and this novel filler can be used to reinforce SBR. A possible reaction mechanism for the effectiveness of this filler is indicated in Scheme 7.

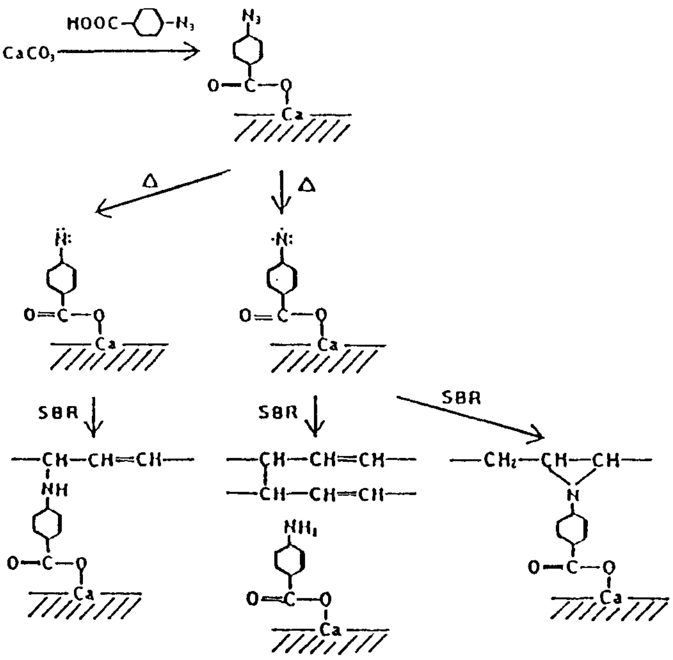
The mechanical properties of SBR loaded with calcium carbonate, modified with *p*-azidobenzoic acid [abbreviated as $CaCO_3$(M)] and unmodified calcium carbonate [$CaCO_3$(C)], were measured. As shown in Fig. 13, above 60 phr $CaCO_3$(C) enhanced the Mooney viscosity significantly, which is not a desirable property. On the other hand, the Mooney viscosity of $CaCO_3$(M) loaded SBR did not increase very much, indicating that the $CaCO_3$ was very well dispersed in the SBR matrix because of the favorable surface modification of the $CaCO_3$. As far as mechanical properties are concerned, $CaCO_3$(M) significantly improves the tensile properties of SBR vulcanizates as shown in Fig. 14.

It was demonstrated that the properties of calcium-loaded rubber, such as good processability and high reinforcing ability, can exist together when the calcium carbonate is properly modified and prepared for the intended application.

Phosphates as Coupling Agents

Another approach to enhance the capability of calcium carbonate as an efficient filler was the use of phosphates as "coupling" agents. The prime targets were alkylphosphates that could react with the calcium carbonate but had groups that could interact with the rubber portion of the composite material. Dialkyl dihydrogenphosphates with such functional groups as olefinic, chloro, methacryloxy, and mercapto groups were synthesized and allowed to react with calcium carbonate fillers suspended in an aqueous medium (Scheme 8).

The phosphate modification of the filler calcium carbonate provided for good filler dispersibility in mineral oil. The physical properties of the vulcanized rubbers



SCHEME 7. Schematic reaction mechanism [14].

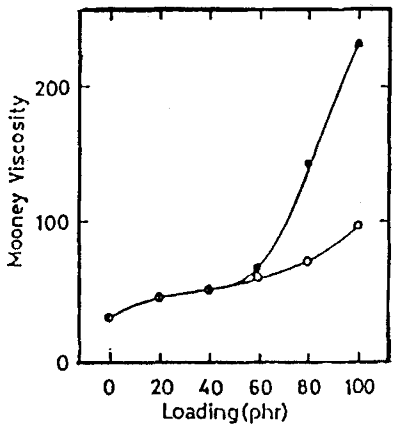


FIG. 13. Mooney viscosity of the calcium-carbonate-loaded styrene-butadiene rubber compound [14]: ○ = calcium carbonate (M); ● = calcium carbonate (C).

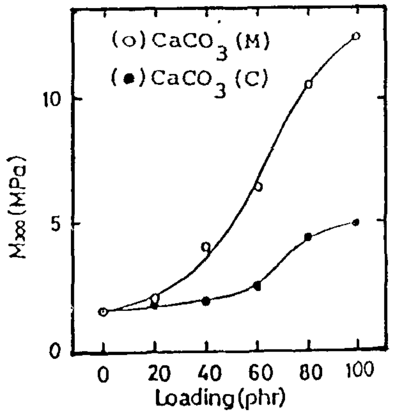


FIG. 14. M_{300} values of calcium-carbonate-loaded styrene-butadiene rubber vulcanizates [14].

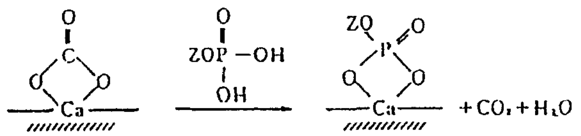
loaded with the modified fillers were found to be influenced by the functional group that had been introduced. For example, in peroxide-cured ethylene-propylene-diene rubber (EPDM), the methacryloxy group was most effective. The mercapto group significantly enhanced the physical properties of sulfur-cured styrene-butadiene rubber (SBR), while a saturated aliphatic phosphate was most effective in both curing systems.

Lignin

Lignin is also a most attractive and inexpensive filler for rubber compositions [16, 17]. Lignin-reinforced rubber compositions have been prepared by coprecipitation. They are valuable for their high mechanical properties and their good aging properties. They are also attractive because they utilize a product available from natural resources and they seem to use a relatively small amount of energy during processing.

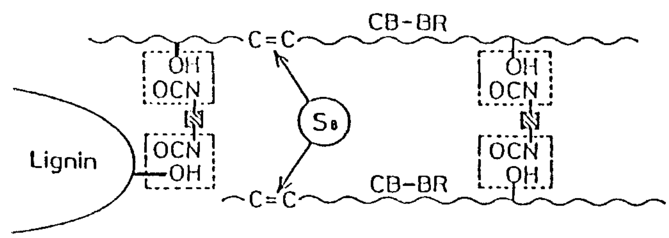
Rubber/lignin compounds have, however, some shortcomings. They have the problems of low processability and large compression set for their vulcanizates.

We have succeeded in improving rubber/lignin compounds by using newly developed chemically modified lignin and by using CB-BR as an additional compo-



Z : $CH_3(CH_2)_7$, $CH_2{-}C(CH_3){-}CO{-}O(CH_2)_3$, $HS{-}(CH_2)_3$, $Cl(CH_2)_3$

SCHEME 8.



SCHEME 9. Schematic curing mechanism [16].

nent for the lignin reinforced vulcanizate. To improve the processability of the rubber/lignin compound without losing the good mechanical properties and the heat-resistant properties, we used CB-BR, which has hydroxyl groups or labile chlorine atoms to make chemical bonds with the surface of the lignin particles (Scheme 9).

Lignin was chemically modified by reacting the phenol groups of lignin with ethylene chlorohydrin which the phenol groups of the lignin into aliphatic hydroxyl groups (Scheme 10),, which then react with CB-BR and SBR to form a modified lignin-reinforced CB-BR vulcanizate as shown in Fig. 15.

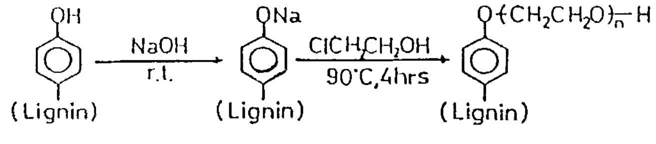
Compounding recipes illustrated in Table 7 were used for the preparation of 5 different kinds of CB-BR vulcanizates: modified and unmodified lignin (ML or L) reinforced CB-BR cured with sulfur with or without a blocked triisocyanate (designated IS or S, respectively) and HAF-loaded CB-BR cured with sulfur (sample C, used as a control).

Table 8 shows the Wallace plasticities of these compounds and the tensile properties of the vulcanizates cured under optimum conditions. As indicated in the table, the sample involving IS-ML showed the best tensile strength at break, T_B. The modulus at 100% elongation, M_{100}, in all lignin-loaded CB-BR vulcanizates was measured. The M_{100} of IS-ML is higher than that of a HAF black-loaded stock, sample C, in spite of the lowest Wallace plasticity, i.e., the lowest viscosity of the uncured stock.

These results indicate that the chemical modification of lignin by ethylene chlorohydrin results in recognizable positive effects for improving the processability and reinforcing of CB-BR.

VULCANIZATION OF RUBBER

Rubber vulcanization has been known and utilized effectively for over 150 years. It consists primarily of the reaction of sulfur, accelerator, and other additives with a linear rubber elastomer to produce a crosslinked rubber network. Amount of



SCHEME 10. Reaction scheme of lignin and ethylene chlorohydrin [16].

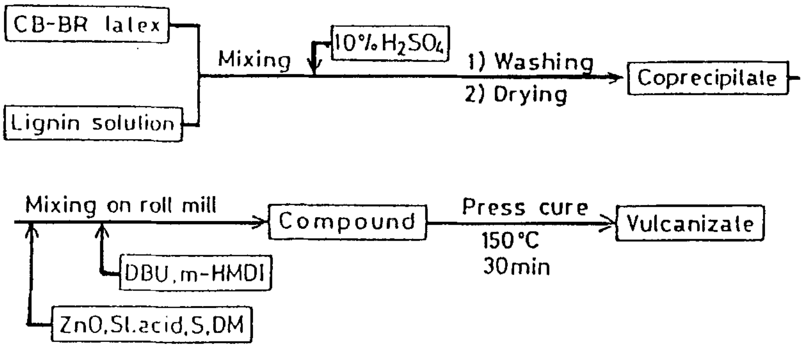


FIG. 15. Preparation of 1-chlorobutadiene-butadiene rubber/lignin vulcanizates [16].

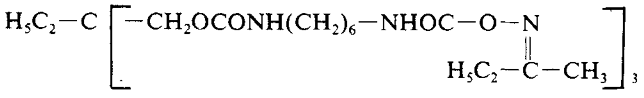
TABLE 7. Compounding Recipes (phr) [16]

	IS	S	C
CB-BR[a]	100	100	100
Lignin[b]	60	60	–
Carbon black	–	–	45
ZnO	5.0	5.0	5.0
Sulfur	2.2	2.2	2.2
Stearic acid	1.0	1.0	1.0
DM[e]	1.7	1.7	1.7
m-HMDI[c]	26.3	–	–
DBU[d]	0.3	–	
Process oil	–	–	5.0

[a] $[OH] = 1.6 \times 10^{-4}$ mol/g.

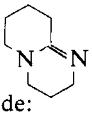
[b] Phenolic $[OH] = 9.27 \times 10^{-4}$ mol/g.

[c] $[NCO]/([OH]_{rubber} + \text{phenolic}[OH]) = 1$. *m*-HMDI (blocked isocyanate):



$$H_5C_2-C\left[-CH_2OCONH(CH_2)_6-NHOC-O-\underset{H_5C_2-C-CH_3}{\overset{}{N}}\right]_3$$

[d] 1,8-Diazabicyclo[5,4,0]undecene-7:



[e] Dibenzothiazyl disulfide:

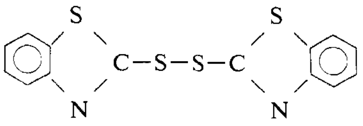


TABLE 8. Physical Properties of Lignin- or Carbon-Black-Loaded 1-Chlorobutadiene-Butadiene-Butadiene Rubber [16]

Cure	Filler	W.P.[a]	M_{100},[b] MPa	T_B,[c] MPa	E_B,[d] %
IS[e]	L[g]	64	5.8	9.5	160
	ML[h]	50	6.1	12.3	220
S[f]	L	74	4.2	10.0	290
	ML	61	4.8	9.0	250
S	C[i]	86	5.4	12.9	190

[a] Wallace plasticity.
[b] Tensile modulus at 100% elongation.
[c] Tensile strength.
[d] Elongation at break.
[e] Isocyanate-sulfur cure.
[f] Sulfur cure.
[g] Unmodified lignin.
[h] Modified lignin.
[i] Carbon black

additives, type of base rubber, vulcanized temperature, and the length of the curing time were found to be essential for the production of the desired final rubber material.

In recent years the pressure to produce the final rubber goods in the shortest possible time has become very important as the most effective way of lowering the production costs and so provide the most competitive price of the final product.

Consequently, high temperature vulcanization at curing temperatures in excess of 170°C has been routinely used and has become a common feature of the "normal" manufacturing process.

Natural rubber (NR) as well as synthetic 1,4-polyisoprene rubber is, however, subject to some thermal degradation at such a high temperature.

As a consequence, the mechanical properties of NR vulcanizates cured at temperatures of 170°C and higher are much lower than those cured at the traditional cure temperatures ranging from 140 to 150°C (Fig. 16) [6]. To avoid lowering or even losing the mechanical properties of these NR vulcanizates, two major developments have occurred: (a) the so-called "efficient" vulcanization systems (EVS) and/or (b) blends of rubber vulcanized with polybutadienes-1,3 with a high vinyl group content.

The "Efficient" Vulcanization System

For vulcanizates which require very high heat and reversion resistance, a vulcanization system is used which is sometimes called an "efficient" vulcanization system (EVS). It uses a very low amount of sulfur but a correspondingly high accelerator concentration.

Figure 17 [18] illustrates a typical example of an EVS and shows that a relatively good match of the tensile properties can be obtained in an EVS. The resistance

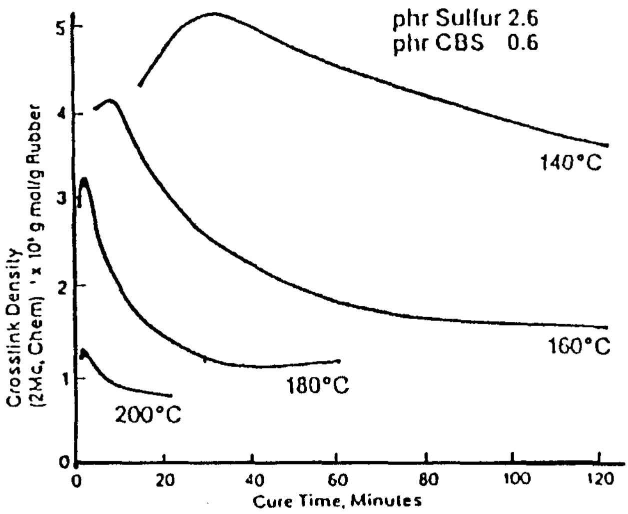


FIG. 16. Influence of the curing temperature on the crosslink density of natural rubber gum [18].

to tensile property revisions can be improved by stepwise reduction of the sulfur levels while increasing the levels of accelerator (Fig. 18) [19]. It would appear that decreases in some of the properties, such as modulus and tensile strength, are due to a high concentration of monosulfidic crosslinks produced and also to a decrease in crosslink density. Monosulfidic crosslinks are not capable of exchanging or rearranging to relieve the highly localized stress associated with the growth of a flaw

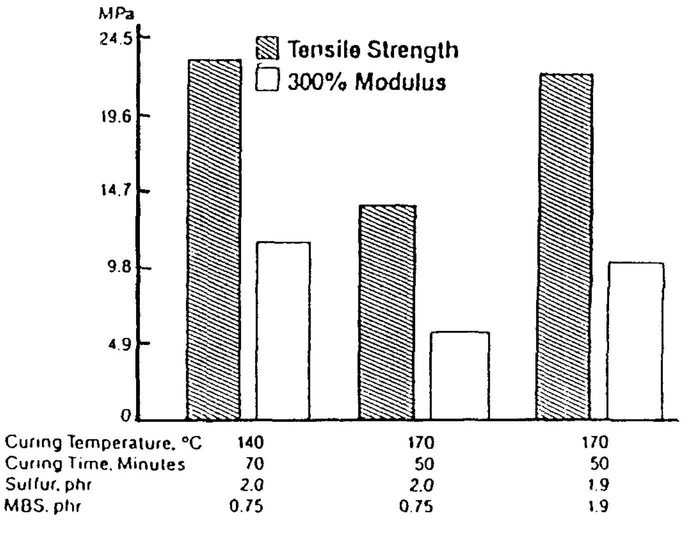


FIG. 17. Effect of the increase of the accelerator level on natural rubber/BR systems [18].

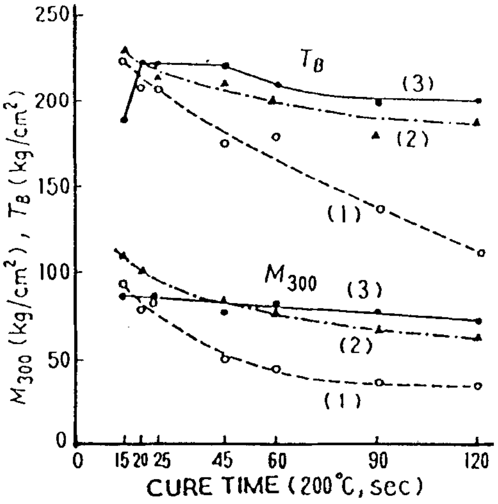


FIG. 18. Improvement in resistance to tensile strength and percent modulus reversion by stepwise reduction of the sulfur levels and the increase of the accelerator levels [19].

produced in the vulcanizate [20]. The fatigue life of the vulcanizate is also improved when the EVS is used, but this aspect must be checked by further research.

Blending

The combination of higher sulfur level and higher cure temperature sharply lowers the tensile strength in NR vulcanizates. On the other hand, BR is relatively unaffected. Hence, the effect is less for blends of NR and SBR, as seen in Fig. 19 [21]. To evaluate the cure reversion of rubber compounds, the reversion parameter R is defined as follows:

$$R = [M_{\max} - (M_{\varepsilon}/M_{\max})] \times 100\,(\%)$$

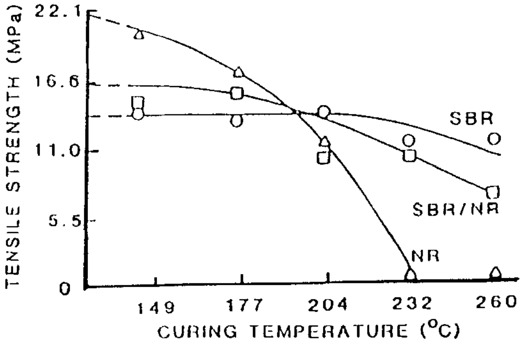


FIG. 19. Tensile strength as a function of curing temperature for natural rubber, styrene-butadiene rubber, and a natural rubber/styrene-butadiene rubber (50:50) blend [21].

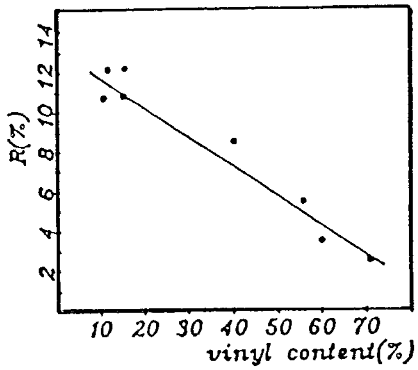


FIG. 20. Effect of vinyl content on the reversion parameter *R* [22].

TABLE 9. The Reversion Parameter *R* of NR/Rubber A [22]

NR/Rubber A	100/0	70/30	50/50	30/70	0/100
R (%)	22.2	8.0	6.1	4.2	0

TABLE 10. The Reversion Parameter *R* of NR/Rubber D [22]

NR/Rubber D	100/0	70/30	50/50	30/70	0/100
R (%)	22.2	12.5	8.5	6.5	5.6

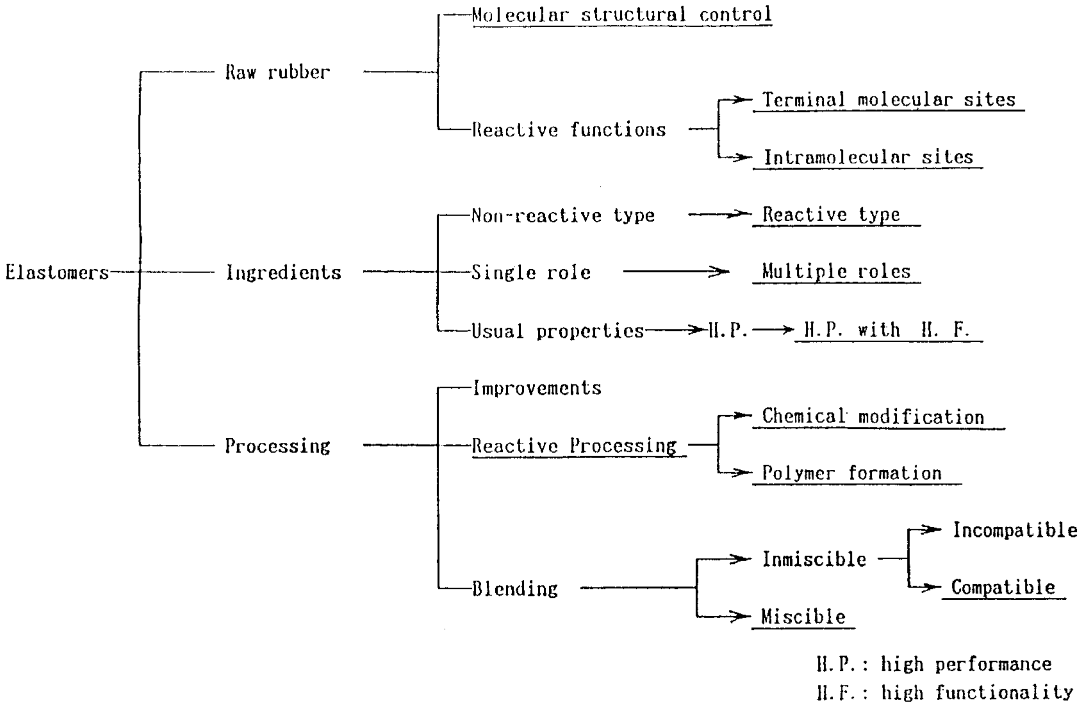


FIG. 21. Future trends in rubber processing (important factors are underlined).

where M_{max} = maximum torque

M_{ε} = torque at a given point where the cure time is 6 times the t_{90}

Lower values of R represent better reversion resistance. The value of R was found to increase with an increase in the vinyl content of the diene rubber (Fig. 20) [22]. On the other hand, the effect of bound styrene in SBR was less pronounced on reversion [22]. The reversion parameters of NR/BR and NR/SBR are listed in Tables 9 and 10, respectively.

From these tables it can be seen that high-vinyl BR dramatically improves the reversion resistance of NR. It is also shown that the blend of NR and high-vinyl BR is miscible, and the crystallization of NR is inhibited at low temperatures while strain-induced crystallization can still occur [23].

CONCLUSIONS

Progress in rubber processing is made by improving the rubber materials as well as their ingredients, and also by the interaction between these two major components to produce high performance rubber goods.

The future trends in rubber processing (Fig. 21) can be summarized as follows:

(1). Production of high performance elastomers by:
  (a). Chemical modification or polymer formation through reactive processing
  (b). Compatible or miscible rubber blends possessing chemical interaction between them
(2). To facilitate the above reaction conditions the improvement of the raw material should be done by:
  (a). For raw material rubber: introduction of reactive functions (preferably) to the terminal sites of the macromolecules or (if not feasible) along the polymer chain
  (b). For novel ingredients: introducing reactive groups as well as multiple roles, for example: high performance with high functionality

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