

Solution-Polymerized Rubbers with Superior Breakdown Properties

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Synopsis

Natural rubber breaks down readily during mechanical mixing, and rubber processors have traditionally made good use of this property. Emulsion SBR rubber breaks down with greater difficulty and some polybutadiene rubbers, not at all. This paper describes a new class of solution elastomers, both polybutadiene and butadiene-styrene copolymers, designed to undergo controlled breakdown during processing. They can be made by reacting active polymer lithium molecules with tin compounds to produce star-shaped molecules containing a central tin atom connected by tin-carbon bonds. When such a product is mixed with an organic (stearic) acid, some of the tin bonds are ruptured and the desired breakdown occurs. The extent of breakdown can be controlled by the mixing conditions and the amount of organic acid employed. There are numerous applications in which these rubbers process more easily and display better properties than conventional rubbers. Data on breakdown under various conditions and physical properties of the compounds are presented in this paper.

In addition to the superior processing characteristics, these products introduce a new concept of elastomer breakdown. The breaking of a polymer chain at a carbon-tin bond by a chemical agent eliminates the need for breaking carbon-carbon bonds by mechanical energy or oxidative degradation. Accomplishing polymer breakdown by a controlled reaction, rather than by conventional means, has long been an unsolved problem of the rubber industry.

INTRODUCTION

Natural rubber breaks down readily during mechanical mixing, and rubber processors have traditionally made good use of this property. Emulsion SBR breaks down with greater difficulty and some polybutadiene rubbers not at all.

This paper describes a new class of solution elastomers, both polybutadienes and butadiene-styrene copolymers, designed to undergo controlled breakdown during processing. They are made by introducing carbon-tin bonds into the main chain. When such a product is mixed with an organic acid, for example stearic acid, some of the carbon-tin bonds are ruptured and breakdown occurs. The extent can be controlled readily by the mixing conditions and the amount of organic acid employed.

Polymers produced by this technique display several important property advantages. They contain sufficient long-chain branching in the raw state

to minimize or even eliminate cold flow during prolonged storage. During mastication, the branched structure and broadened molecular weight distribution contribute to better mixing. After compounding, most of the long branches have been separated from the chains; and the compound displays lower Mooney viscosity and the good mold flow characteristics of a linear, narrow molecular weight distribution polymer. The linearity and narrow distribution also afford advantages in vulcanizate properties, particularly in hysteresis, when compared to corresponding polymers containing strong permanent branches which persist through mixing and vulcanization.

Preparation of Elastomers Containing Carbon-Tin Bonds

The polybutadiene and butadiene-styrene copolymers for this study were produced by solution polymerization with butyllithium initiation, a system well characterized kinetically¹ and one now well known to produce "living" polymers. Several methods for the introduction of metal or metalloids into the polymer chains have been described in the literature.^{2,3} In this section of the paper, we restrict ourselves to the laboratory and pilot plant preparations in which a branching agent, tin tetrachloride, was reacted with an active or "living" polymer lithium. The experimental technique is described by Zelinski and Wofford.⁴

Small samples of the experimental polymers were prepared by means of a bottle polymerization technique described in the literature.^{1,4} Larger samples for compounding studies and extensive testing were produced in pilot plant reactors. Some products, available commercially under the Solprene tradename, were also employed in the processing and vulcanization tests.

Although a considerable number of reagents can be used as terminating reagents to produce branched polymers, only a limited number yield polymers containing organometal bonds displaying the desired balance of stability and cleavability. One such linkage is the carbon-tin bond.

The chemistry involved in the preparation and breakdown of the polymers is illustrated in the following reaction sequences:

1. Polymerization: $R\text{Li} + \text{monomer} \rightarrow \text{polymer-Li}$
2. Termination: $4 \text{ polymer-Li} + \text{SnCl}_4 \rightarrow (\text{polymer})_4\text{Sn} + 4 \text{ LiCl}$
3. Breakdown: $(\text{polymer})_4\text{Sn} + 4 \text{ RCOOH} \rightarrow 4 \text{ polymer-H} + (\text{RCOO})_4\text{Sn}$

The order of ease of cleavage of $R_4\text{Sn}$ compounds by electrophilic reagents is allyl > vinyl > phenyl > alkyl. The conditions required to accomplish complete cleavage are excess reagent, elevated temperature, and time. The particular susceptibility of allyl groups to cleavage is attributed to an SE 2' mechanism.⁵ The conditions described in this report are especially suited to cleavage of the carbon-tin bond in the polymers described.

In the remaining sections of this report, we will present laboratory data to illustrate the ready control of breakdown possible with these new elas-

tomers, and we will cite a few examples of their use in commercial applications.

EXPERIMENTAL

Addition of a tin compound to a living polybutadiene-lithium system in hydrocarbon medium results in a rapid reaction with elimination of the corresponding lithium compound and the formation of carbon-tin bonds. Depending upon the stoichiometry between the polymer-lithium and the tin compound, various structures are produced, ranging from linear molecules to star-shaped molecules in which four linear chains are attached to a central tin atom. The reaction is rapid and free from side reactions, in contrast to molecular weight jumping based on cationic polymerization agents. The latter reaction is characterized by crosslinking and gel-forming reactions simultaneous with scission reactions which produce low molecular weight fragments.⁶

Because polybutadiene terminated with stannic compounds contains long-chain branching, there is a dramatic reduction in cold flow. Data in Table I illustrate this effect. Here, a series of linear polybutadienes of about 10 Mooney viscosity and lower (ML-4 at 100°C) was prepared by polymerization with butyllithium initiation. At quantitative conversion,

TABLE I
Cold Flow Properties of Tin-Coupled Polybutadiene

Recipe						
	1,3-Butadiene, parts					100
	Cyclohexane, parts					780
	<i>n</i> -Butyllithium, mmoles					variable
	Stannic chloride, mmoles					variable
	Temperature, °C					50
	Conversion, %					100
	Time, hr					3 + 16*

Coupling Data						
BuLi charged, mhm ^d	Effective BuLi level, mhm	SnCl ₄ , mhm	Parent polymer ^b		SnCl ₄ -terminated polymer ^b	
			η_{inh}	Cold flow, ^c mg/min	η_{inh}	Cold flow, mg/min
1.0	0.4	0.10	1.66	104	2.80	0
1.2	0.6	0.15	1.33	171	2.44	0
1.4	0.8	0.20	1.31	357	2.36	0
1.6	1.0	0.25	1.12	613	2.18	0

* After 3 hr of polymerization to 100% conversion the SnCl₄ was added and the coupling reaction was continued for 16 hr at 50°C. Polymers were protected with 1.0 phr 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol) and coagulated in isopropanol.

^b None of the polymers contained gel.

^c Milligrams of rubber forced through a 1/4-inch orifice at 3.5 psi at 50°C.³

^d Millimoles/100 g monomer.

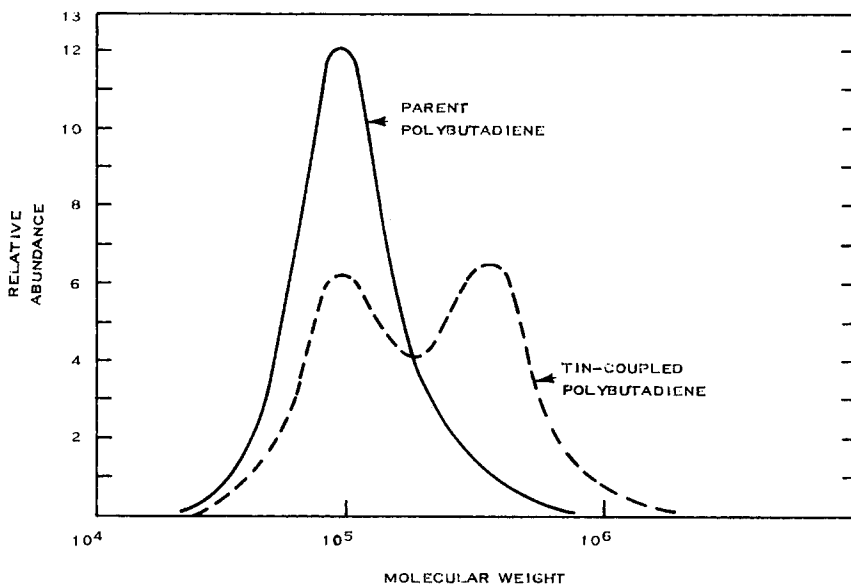


Fig. 1. Molecular weight distribution of parent and tin-coupled polybutadiene.

the polymerizations were sampled for reference, then terminated by addition of a tin compound. The inherent viscosity data in Table I show that molecular weight was increased by tin termination, all polymers were gel free, and the cold flow was reduced from very high values (ranging from 100 to 613 mg/min) to zero.³ Typical commercial polybutadienes display cold flow values ranging from 0.1 to 2 mg/min in this test.

Further evidence of the presence of tin-branched polybutadiene was obtained by purposely preparing a polybutadiene containing roughly equal fractions of linear and branched rubber. This was accomplished by polymerizing with sufficient butyllithium to produce about 10 ML-4 Mooney viscosity polybutadiene, then terminating by adding sufficient stannic salt to increase the Mooney viscosity to 52 ML-4. Samples of both the 10 ML-4 Mooney parent and the 52 ML-4 Mooney product were fractionated on the Waters gel permeation chromatograph. The results are shown in Figure 1. The parent polymer shows a single narrow peak, while the terminated polymerization shows two peaks, one corresponding to the molecular weight of the parent polymer, the second to approximately four times the molecular weight of the parent, when the molecular weight is determined by the use of a universal calibration curve proposed by Benoit and associates.⁷

RESULTS

Polymer Breakdown Experiments

The 52 ML-4 polybutadiene was also employed in mastication studies to investigate breakdown characteristics in the presence of stearic acid. It

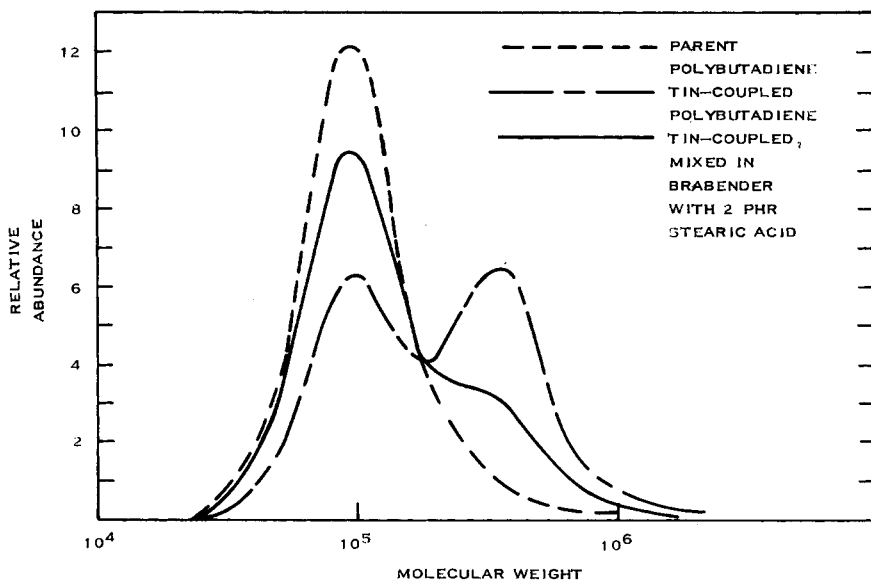


Fig. 2. Molecular weight distribution of parent, tin-coupled, and Brabender broken down polybutadiene.

was mixed in a Brabender Plasti-Corder at 150°C under vacuum in the presence of 2 phr of steric acid for a period of 2 min, then held for an additional 5 min without mixing. The molecular weight distribution of the polymer before and after this treatment (Fig. 2) clearly shows that most of the high molecular weight fraction was broken down selectively, regenerating most of the parent polymer. Under milder conditions, for longer periods of time, still greater recovery of the parent polymer peak occurred.

Selective breakdown is also apparent from data in Table II on molecular

TABLE II
Viscosity and Molecular Weight Data

Polybutadiene	Mooney viscosity, ML-4	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	Heterogeneity index
Parent	10	118	89	1.33
Product	52	249	138	1.80
Broken down	17	169	102	1.66

weight and Mooney viscosity of the 10 Mooney parent polybutadiene, the 52 Mooney product, and the 52 Mooney product after mastication in the presence of 2 phr of stearic acid at 150°C.

These experiments are strong confirmation that reaction sequence presented earlier does indeed occur.

Effect of Parent Mooney on Breakdown

Three polybutadienes originally prepared to parent Mooney viscosities of approximately 10, 20, and 30 were coupled by different amounts of tin reagent to a Mooney of about 50. The coupled polymers were mixed with 2 phr of stearic acid for 2 min on a cold mill, then each mixture was broken down in the Banbury at 121°C and 30 rpm for increasing lengths of time. At each time, portions were sampled for viscosity measurements. For control, a 57 Mooney viscosity linear polybutadiene was treated in an identical manner. The linear 57 Mooney polybutadiene control decreased only slightly in Mooney viscosity during mastication, and much of the decrease was caused by plasticizing action of the stearic acid. The tin-coupled polymers, in contrast, displayed rapid breakdown in the first few minutes of mixing. At longer mix times, each of the three tin-coupled polybutadienes approached a limiting Mooney viscosity which was dependent upon and usually higher than the parent Mooney viscosity. The polybutadiene prepared from the 10 Mooney viscosity parent decreased 34 Mooney points during mastication with stearic acid, the polybutadiene produced from a 30 Mooney parent decreased by 22 points, while the linear control polybutadiene dropped only 4 units under the same conditions. The Mooney viscosity-time of mixing curves are plotted in Figure 3, and a summary of the

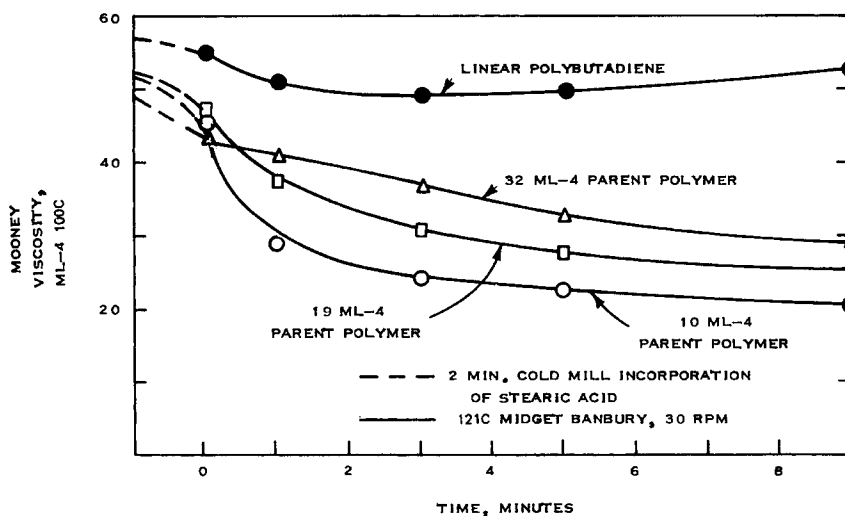


Fig. 3. Effect of parent polymer Mooney on Banbury breakdown in presence of 2 phr stearic acid of tin-coupled polybutadiene

experimental data is given in Table III. Included in this table are compounded Mooneys for the tin-coupled polymers mixed in a standard tread formulation. The latter data illustrate that the tin-containing polybutadienes undergo controlled breakdown in the presence of stearic acid in a practical tread stock formulation.

TABLE III
Banbury Breakdown of Tin Containing Polybutadienes
Coupled to a Constant Mooney

Parent polymer		Tin-coupled polymers		Broken-down polymer ^a			Com- pounded Mooney, ML-4 ^c
η_{inh}	ML-4	η_{inh}	ML-4	η_{inh}	ML-4	Power, ^b watt	
1.45	10	2.09	53	1.65	19	345	34
1.72	19	2.25	53	1.80	24	285	52
2.03	32	2.28	51	1.92	29	225	76
2.36	57	—	—	2.29	53	15	106

^a See text for mixing conditions.

^b Power drop = (maximum wattage) - (wattage after 10 min).

^c Tread formulation: rubber, 100; IRB, 50; ZnO/stearic acid, 3/2; Dutrex, 10; sulfur/Santocure NS, 1.75/0.8.

Effect of Variable Stearic Acid and Temperature

Breakdown of polymers containing carbon-tin bonds is affected by the amount of stearic acid and by the temperature of mixing. This is shown in Figures 4 and 5 for experiments with Solprene 1204, a 75/25 butadiene-

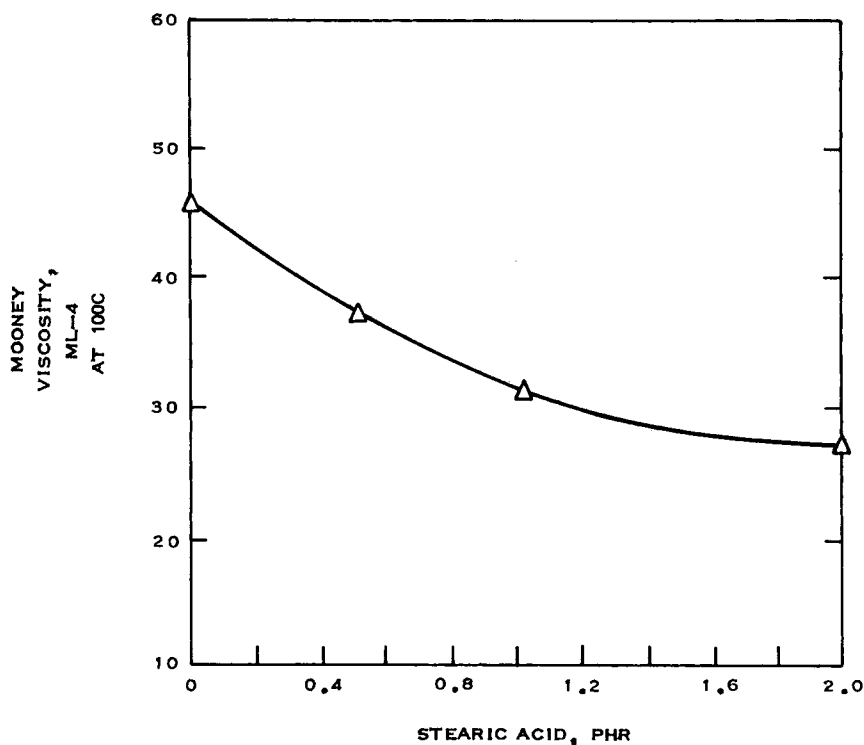


Fig. 4. Effect of stearic acid level on breakdown of Solprene 1204 rubber. All stocks mixed 5 min on 90.5 C roll mill.

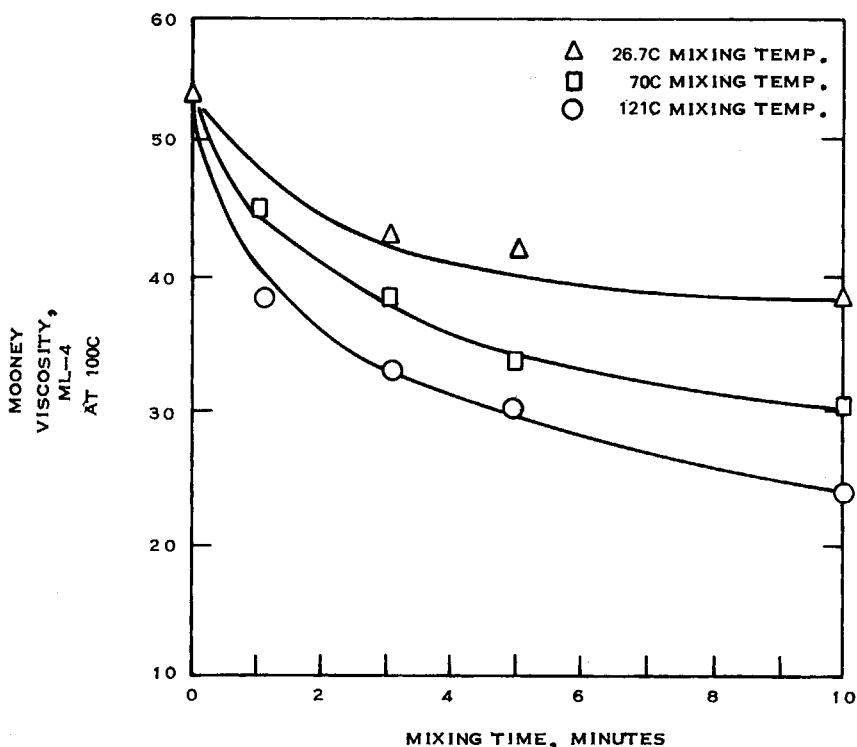


Fig. 5. Effect of mixing temperature on breakdown of Solprene 1204 rubber: (Δ) 26.7 C mixing temp; (\square) 70 C mixing temp; (\circ) 121 C mixing temp. All stocks mixed in midget Banbury, 60 rpm.

styrene solution SBR. When more than the two parts of stearic acid are used (Fig. 4), a further reduction in Mooney is observed; however, this is due primarily to the plasticizing action of the fatty acid rather than polymer breakdown. On a molar basis, 2 phr of stearic acid exceeds the equivalence of carbon-tin bonds in the rubber. Figure 5 illustrates the difference in breakdown at various mixing temperatures. The rate increases with temperature and most of the reaction is completed in the first 5 min.

Comparison with SBR

The butadiene-styrene solution random copolymers included in this report are similar to emulsion SBR in many respects, but several significant differences exist. One of these is breakdown in the presence of acid. A comparison of SBR 1500 and Solprene 1204 rubber is shown in Figure 6. As can be seen, Mooney reduction of Solprene 1204 copolymer is quite rapid during the first 5 min and then tapers off. In the absence of stearic acid, the solution polymer behaves much like SBR 1500 with stearic acid present. In formulations in which a minimum amount of breakdown is preferable,

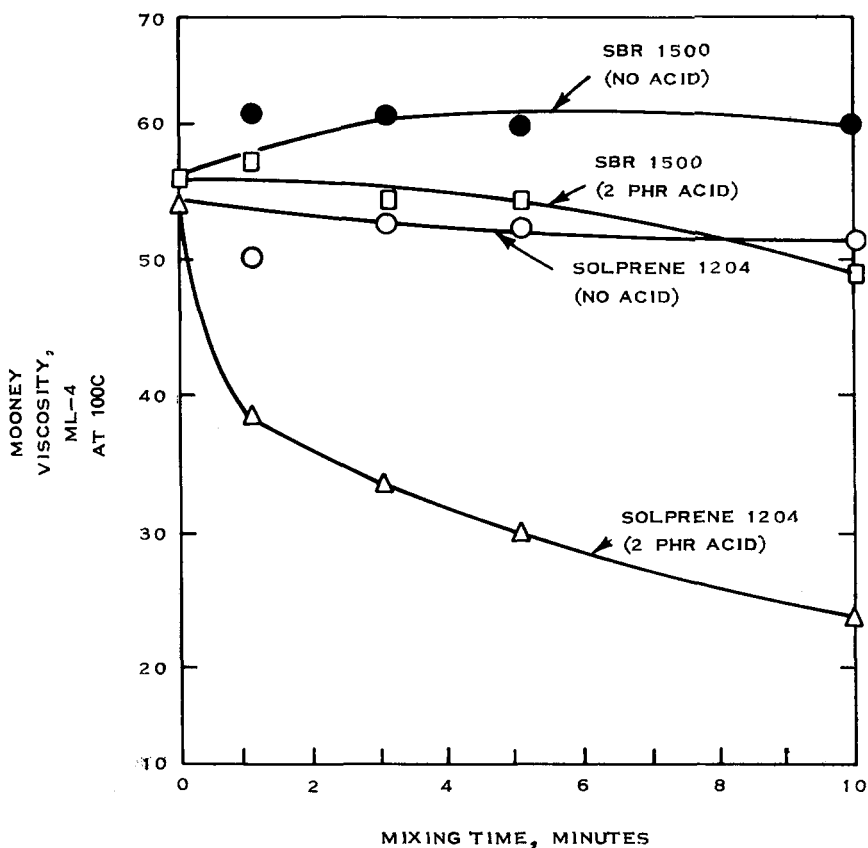


Fig. 6. Breakdown of Solprene 1204 rubber in the presence of stearic acid. All stocks mixed at 121 C, 30 rpm in midget Banbury.

stearic acid can be withheld from the compound until carbon black and softener are incorporated.

Breakdown Promoters

Breakdown promoted by organic acids can also be demonstrated by comparing several acids with conventional peptizers and other additives used in rubber systems. The various reagents were added to the commercial Solprene 1204 rubber and blended on a roll mill for 5 min at 90.5°C prior to sampling for Mooney viscosity determinations (Table IV).

The data in Table IV show an obvious difference in promotion of breakdown between the organic acid and some commonly used peptizers under the conditions of the experiment. The aliphatic acids behaved alike. Some of the commercial organic acid retarders could be used as combination retarders and peptizers in the Solprene rubbers specifically designed for breakdown by organic acids.

TABLE IV
Various Materials as Breakdown Promoters in Solprene 1204 Rubber

Additive	phr	Composition	Mooney, ML-4 at 100°C
None	—	—	45
Stearic acid	1	Stearic acid	26
Lauric acid	2	Lauric acid	29
Sorbic acid	1	Sorbic acid	28
Retarder W	1	Salicylic acid	22
Benzoic acid	1	Benzoic acid	31
Resin 731	2	Disproportionated wood resin	38
Pepton 22	2	Amidophenyl disulfide peptizer	44
Peptide 65	2	Amidothiophenate plasticizer	46
RPA #6	2	Chlorothiophenol peptizer	43
Aberol ST 137X	1	Phenol-formaldehyde resin	40
Flexamine	1	Amine-type antioxidant	44
Ionol	1	Phenolic-type antioxidant	44

From the data in Table IV it is apparent that conventional rubber peptizers were much less effective breakdown reagents under the mild conditions of this experiment.

Physical Properties

We have shown in the preceding sections of this study that these tin-branched elastomers undergo selective breakdown in the presence of an organic acid, regenerating linear relatively narrow molecular weight polymers after compounding. This type of product displays excellent vulcanizate properties. A comparison of tread vulcanizate properties of three tin-branched polybutadienes, a polybutadiene branched during polymerization with divinylbenzene (DVB), and a linear polybutadiene are presented in Table V.

TABLE V
Vulcanizate Properties of Polybutadienes in a Tread Formulation^a

	Tin-branched polybutadiene			DVB-branched	Linear
	A	B	C		
Parent Mooney, ML-4	19	32	40	—	—
Product Mooney, ML-4	53	51	67	60	57
Cold flow, mg/min	0.22	—	0.71	0.8	8.6
Compound Mooney, ML-4	52	76	92	98	106
Tensile, psi	2330	2340	2510	2280	2230
300% Modulus, psi	950	1090	1000	1270	1130
Elongation, %	520	480	500	410	445
Heat buildup, $\Delta T^\circ\text{F}$	61	55	55	64	62

^a Rubber, 100; IRB No. 2, 50; ZnO, 3; Dutrex 726, 10; stearic acid, 2; sulfur, 1.75; Santocure NS, 0.8.

It is apparent from the data that the tin-branched polybutadienes are superior with regard to cold flow, processability, and heat buildup in comparison to either the divinylbenzene-branched polybutadiene or the linear control. The data also illustrate that the degree of breakdown, as measured by compound Mooney viscosity, is subject to control. Thus, while there is little difference in the vulcanizate properties of the three tin-branched polybutadienes in Table V, the compound Mooney viscosities range from 52 to 92, almost a 50% variation.

Applications

A number of tin-containing elastomers are produced commercially by Phillips Petroleum Company under the Solprene tradename. Solprene 200 polybutadiene can be used advantageously in tire tread formulations in combination with SBR or natural rubber. The selective breakdown properties of Solprene 200 in such application generally permits shorter mix cycles without sacrificing dispersion or physical performance. Among the butadiene-styrene copolymers, Solprene 1204 displays excellent tire performance in comparison to emulsion SBR 1500.

Another butadiene-styrene copolymer, Solprene 1206, has been tailored specifically to undergo rapid breakdown in the presence of organic acid to yield low Mooney viscosity compounds for sponge rubber fabrication. A typical formulation for sponge rug underlay comparing Solprene 1206 and SBR 1506 is shown in Table VI. Even though the Solprene 1206 formula-

TABLE VI
Solprene 1206 and SBR 1506 in Sponge Rug Underlay Compounds

	Parts	
Solprene 1206	100	—
SBR 1506	—	100
Whiting	225	165
Clay	50	30
Circo light oil	62.5	60
Zinc oxide	4	4
Organic acid	10	12
MBTS	—	2.5
MBT	2	—
Methyl zimate	1	1
Sulfur	5.5	4
Sodium bicarbonate	—	15
Unicel S	12	—
Petrolatum	15	—
Plastogen	—	2
Silene EF	3	—
	490	395.5
Mooney viscosity, ML-4, 100°C	4	5
Surface appearance	smooth	rough
25% Compression deflection, lbs	4.2	3.5

tion is more highly loaded, it displays lower compound Mooney viscosity and better physical properties than the SBR stock.

CONCLUSIONS

The synthesis of elastomers containing tin-carbon bonds capable of controlled scission by means of organic acid introduces a new concept into elastomer breakdown. The selective cleavage of the carbon-tin bond in these new rubbers produces compounds with linear narrow molecular weight distribution and the physical property advantages associated with this structural feature. Breaking the tin-carbon bond selectively by chemical reaction eliminates the need for conventional carbon-carbon bond breakdown by mechanical energy or by means of conventional peptizers.

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