

Behavior of *cis*-Polybutadiene During Mastication

GERARD KRAUS and K. W. ROLLMANN, *Phillips Petroleum Company, Research and Development Department, Bartlesville, Oklahoma*

Synopsis

Cold mastication of natural rubber in presence of oxygen leads to scission by a shear mechanism with subsequent stabilization of the free radicals by oxygen, while at high temperatures oxidative scission becomes the dominant mechanism. Studies of the behavior of *cis*-polybutadiene reveal that similar reactions are effective, but occur at much reduced rates. Shear degradation is particularly difficult to achieve in typical *cis*-polybutadienes. This is related to the molecular weight distribution of these polymers which usually lack the very high molecular species most subject to shear-induced degradation, in agreement with the theory of F. Bueche. It is shown that when such a high molecular weight fraction is supplied, shear breakdown may be realized. All *cis*-polybutadienes undergo oxidative breakdown at high temperatures, the scission rate becoming appreciable above 140°C. A number of oxidation catalysts have been found which markedly increase the scission rate without leading to a correspondingly large increase in cross-linking. Significant improvements in processing may be realized in this manner.

I. INTRODUCTION

Compounding studies have shown *cis*-polybutadiene to be difficult to break down by mastication.¹ This very striking difference relative to *cis*-polyisoprene, which breaks down readily, is one of the most characteristic properties of *cis*-polybutadiene. In the present report we hope to demonstrate that although the same basic mechanisms are operative in both polymers it is the higher resistance of *cis*-polybutadiene to scission by shear which accounts for much of the difference in behavior. The breakdown observed in *cis*-polybutadiene on hot mixing in the presence of oxygen is a thermal oxidative phenomenon not primarily related to shear.

II. THEORETICAL BACKGROUND

A fairly good picture of polymer breakdown has been built up largely around the behavior of natural rubber.²⁻⁵ When *cis*-polyisoprene (natural or synthetic) is subjected to shear at low temperatures mechanical scission occurs. Since the stress is transmitted to the polymer chain through entanglements it increases greatly from the end toward the center of the chain. The result is that mechanical scission is not random, but occurs more often in the vicinity of the center of the molecule. The free radicals produced in the primary act of scission can attack the chain and will do so in the absence of reagents (like oxygen) which are capable of stabilizing

them. Consequently cold milling produces a permanent reduction in molecular weight only when carried out in the presence of some oxygen or some other radical acceptor. As the temperature of mastication is raised the solubility of oxygen in the rubber decreases, as does the viscosity. Oxygen-stabilized shear degradation becomes less pronounced, and the breakdown rate decreases. At yet higher temperature, scission becomes wholly oxidative—in fact it takes place without shear, as in the aging of raw or vulcanized rubbers. This scission process is random, but in the presence of shear some directive influence toward the chain center persists.

A quantitative theory of mechanical degradation has been recently published by F. Bueche.⁶ This theory is not readily applied quantitatively to experimental data, but its qualitative predictions are of extreme interest, particularly for the behavior of *cis*-polybutadiene. Based on the concept of stress transmission and concentration by entanglements, the theory leads to the following principal results. The rate of breakdown is given by

$$N = N_0 e^{-P\omega t} \quad (1)$$

where N is the number of chains unbroken at time t , N_0 the original number of chains, P the probability of a chain breaking [assumed constant in eq. (1)], and ω the bond vibration frequency.

$$P \cong K e^{-(E - F_0\delta)/kt} \quad (2)$$

where

$$K = (\omega Z/4)(\pi kT/F_0\delta)^{1/2}$$

E is the energy needed to break a bond, F_0 the force acting on the bond, δ the distance through which the bond will stretch before breaking, and Z is the number of links per chain, the remaining symbols having their usual meaning. The quantity K is a "near-constant" relative to the very rapidly varying exponential function. The key quantity is F_0 , which is given by the following relation:

$$F_0 = (18/\rho N_a)\eta\dot{\gamma}(\bar{M}_t/R_t^2)(M_e/M_0)^{1/2}(M/\bar{M}_t)^2l \quad (3)$$

Here ρ is the density, N_a is Avogadro's number, η the viscosity, $\dot{\gamma}$ the shear rate, \bar{M}_t an average molecular weight intermediate between the weight and Z -average, R_t the root-mean-square end-to-end distance of the polymer molecules, M_e the molecular weight between entanglements, M_0 the molecular weight of the monomer unit, and l the length of a chain link. The molecular weight M , without subscript, refers to the molecule which supports F_0 at its center. It will prove instructive to refer back to these relations in interpreting the results obtained in this study.

The chemistry of the two breakdown processes, shear and oxidative, is undoubtedly related.⁷ The important difference is that in shear breakdown mechanical forces initiate scission and oxygen stabilizes the chain ends, whereas in oxidative degradation the molecules cleave at peroxide sites originally formed by oxidation of the main chain.⁸ Since the ROO·

radicals formed by reaction of oxygen with shear-generated radicals are sources of hydroperoxides, oxidative degradation may be expected to augment shear-initiated breakdown. Similarly, the activation energy for scission of the cyclic peroxides formed in the chain during oxidation will be lowered by shear. In natural rubber the result of this overlapping is that one dominant mechanism leads continuously into the other as temperature is increased. We shall show that in *cis*-polybutadiene a much sharper distinction between the two mechanisms can be drawn.

III. EXPERIMENTAL

Polymers

The rubber used in most of the present work was a commercial *cis*-polybutadiene (Cis-4, Phillips Chemical Company) with the properties given in Table I.

TABLE I

Mooney viscosity, ML-4	47
Inherent viscosity (toluene, 25°C.)	2.54
Gel, %	0
<i>cis</i> -Configuration, %	95
Antioxidant (American Cyanamid AO.2246), %	0.5

The bimodal molecular weight distribution polymer used in the study of shear breakdown was a special research sample. Except for its unusual molecular weight distribution it differed in no important respect from the commercial polymer. This rubber had a Mooney viscosity of 47 ML-4 and an inherent viscosity η_{inh} of 3.95. Its principal molecular weight fractions were: 16.4%, η_{inh} 10.5; 83.6%, η_{inh} 2.66.

Mastication Experiments

The mastication experiments were carried out in a Brabender Plastograph fitted with a vacuum chamber. The Plastograph continuously records the torque on the mixing rotors. The instrument was capable of being operated at a pressure of ca. 1 mm. mercury. The jacket temperature at the beginning of each run could be controlled quite accurately, but at the mixing speeds useful in mastication the heat generated could not be dissipated rapidly enough to maintain isothermal conditions. The stock temperature was therefore recorded continuously from a thermocouple located at the bottom of the mixing head. Most mastication experiments were conducted for 6 min., this time being fairly representative of normal commercial operations. In most cases trends were clearly established in the first 1-2 min. When this was not the case, longer mastication times were investigated.

In experiments with black stocks the carbon black and other ingredients were preblended on a cool roll mill before starting the Plastograph tests. This was done to eliminate the black incorporation stage from the torque-time record.

Low Shear Extrusion Test

This test, designed to detect small changes in rheological properties, consisted in measuring the polymer extrusion rate at steady state from an orifice of 0.25 in. diameter and 0.107 in. length under a pressure of 3.5 psi.

Stress Relaxation

Stress relaxation experiments to demonstrate scission in the absence of shear were conducted using acetone-extracted, peroxide-crosslinked (0.2 phr dicumyl peroxide) gum. Spring relaxometers were used and all strips were prerelaxed 16 hr. *in vacuo* at 25°C. to eliminate physical relaxation phenomena during the test. For experiments on the effects of chemical plasticizers, the latter were introduced into the finished vulcanizates by impregnation from toluene solution. Relaxation experiments with black vulcanizates were run on unextracted samples. All stress relaxation measurements were made at 50% elongation and 100°C.

Sedimentation Velocity

All determinations of the distribution of sedimentation coefficients were carried out by Dr. R. Q. Gregg with a Spinco ultracentrifuge. The measurements were made at a single concentration in *n*-hexane (3 g./l.). As the data were not extrapolated to infinite dilution the various distribution curves obtained should be regarded as relative only. There is at present no satisfactory method known for the extrapolation of the sedimentation coefficient to zero concentration. Details of the sedimentation experiments will be reported elsewhere.

TABLE II

	Parts
Polymer	100
HAF Black ^a	60
Highly aromatic oil ^b	10
Lauric acid	2
Zinc oxide	3
Sulfur	Variable ^c
Accelerator	Variable ^c
Antioxidant ^d	1

^a Philblack 0.

^b Philrich 5.

^c As shown in Tables V and VI, respectively.

^d Flexamine.

Property Evaluations

Conventional methods were used in all physical property evaluations on tread-type vulcanizates. These have been described in other publications from these laboratories.⁹ The basic compounding recipe used is given in Table II.

IV. RESULTS AND DISCUSSION

Mastication of *cis*-Polybutadiene in Absence of Oxygen

Mastication in absence of oxygen furnishes a sensitive test for thermally or shear-induced chain scission. If scission occurs, the resulting free radicals will either recombine or will attack other polymer chains leading to branched and crosslinked structures. It is extremely unlikely that *all* chain radicals will recombine promptly so that some effect on polymer

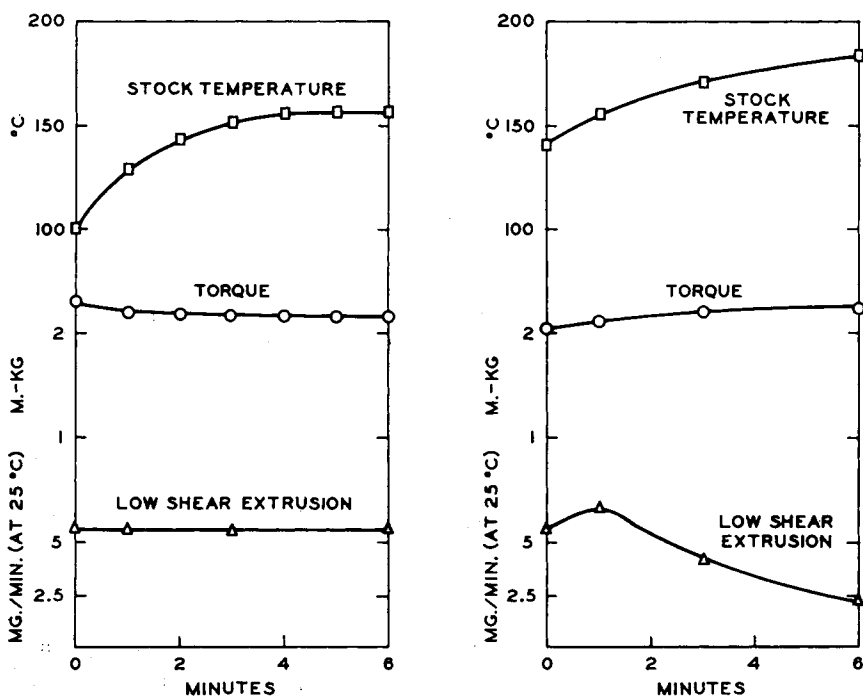


Fig. 1. Mastication of *cis*-polybutadiene *in vacuo* at 100 and 140°C. jacket temperature.

structure will become apparent. Since the primary act (scission) is a degradative one, but is followed by an aggregative one and since slight amounts of branching have no great effect on dilute solution viscosity, the latter may not change at all. However, the presence of branched structures will result in a reduction in low shear flow.¹⁰ On the other hand, if scission never occurs, then neither inherent viscosity nor bulk viscosity will be affected.

Figure 1 shows the response of a 47 ML-4 *cis*-polybutadiene (inherent viscosity = 2.54, gel = 0) to mastication *in vacuo* at 100 rpm in the Brabender Plastograph at two jacket temperatures. Also included are the results of low shear extrusion tests on samples taken at 0, 1, 3 and 6 min. mastication time. At the lower temperature the torque on the rotors decreases slightly as the temperature rises (isothermal mixing at this high rotor speed is impossible with this instrument), but the extrusion data taken at 25°C. show no change. At the higher temperature the torque increases against the temperature trend and the extrusion data clearly indicate a change in polymer structure. Significantly, no gel was formed in either experiment and the inherent viscosity (in toluene), while showing no change in the 100°C. experiment, increased only to 2.59 at the end of the 140°C. test. This behavior is typical of *cis*-polybutadiene and has been repeated many times with different samples.

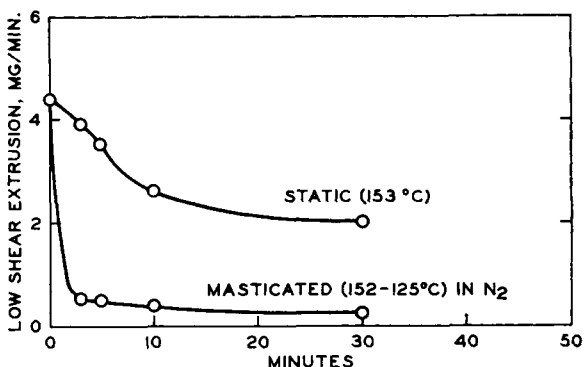


Fig. 2. Mastication vs. static heating.

These results prove that at the lower temperature the polymer survives mastication essentially unchanged. This can also be demonstrated by repeated Plastograph tests on the same sample. During anaerobic mastication below 100°C. the torque depends only on the temperature and mixing speed. At the higher temperature the data clearly suggest crosslinking. The slight initial decrease in melt viscosity (increased extrusion rate) suggests that scission by shear occurs, the radicals being stabilized by traces of adventitious free radical acceptors. Following this initial stage, attack of the free chain radicals on neighboring molecules predominates to form branched structures. That shear contributes to the toughening of the polymer can be demonstrated by comparisons of static heating versus mastication. Such an example is shown in Figure 2. Without shear some thermal crosslinking is apparent, but it is obviously augmented by mastication.

It is interesting to inquire about the nature of the bond being broken. If we assume that the scission of 2% of the chains is the minimum change detectable, that our polymer molecules have a molecular weight of 400,000

and that this change occurs in about 10^2 sec. (see Fig. 1), the fraction of bonds which will have to break per second is roughly 7×10^{-9} . This is also the probability that a particular bond will break in 1 sec. and is equal to the product of the bond vibration frequency (ca. 10^{12}) and $e^{-E_t/kT}$, where E_t is the thermal energy required to break the bond. Hence

$$e^{-E_t/kT} = 7 \times 10^{-21}$$

or

$$\frac{E_t}{kT} = 46.5$$

At 430°K. this amounts to $E_t = 40$ kcal./mole. It thus appears that the bonds broken thermally are not C—C bonds (ca. 60 kcal./mole), but "weak" links, possibly resulting from oxidation. At 100°C. using the above figures, the rate of thermal scission and ensuing crosslinking reactions would be of the order of 1000 times smaller which is consistent with the total absence of any detectable effects. Also, by eq. (2), a shear contribution, $F_0\delta$, of about 1 kcal./mole would be sufficient to increase the probability of chain scission roughly threefold. The question arises, why as a result of increased viscosity $F_0\delta$ does not increase sufficiently to cause scission at lower temperatures. Rheological measurements in these laboratories have shown that the viscosity of *cis*-polybutadiene slightly more than doubles between 430 and 373°K. By eqs. (2) and (3) it may readily be shown that such an increase in shear energy would not be sufficient to compensate for the reduction in thermal energy.

Unfortunately all the quantities in eq. (3) are not known with sufficient accuracy to allow an estimate of $F_0\delta$ to be made by direct calculation. Substitution of plausible values, however, does indicate the magnitude of $F_0\delta$ to be of the order of 10^3 cal./mole for the example cited. The experimental data thus appear to be in harmony with the Bueche theory.

Mastication in the Presence of Oxygen

In view of the above discussion one would not expect typical *cis*-polybutadiene to break down significantly by the oxygen-stabilized shear mechanism at temperatures substantially below 150°C. However, above 100°C. breakdown may occur by the oxygen initiation mechanism. The temperature at which oxidative scission becomes rapid has been determined by stress relaxation measurements of carefully extracted peroxide gum vulcanizates. The results are shown in Figure 3. We observe that purely thermal scission is negligible below 120°C. Oxidative scission is insignificant below 80°C., but becomes quite rapid above 120°C. The polymer should, therefore, be unaffected by mastication in presence of oxygen below ca. 100°C. since neither shear nor oxidation will cause scission at an appreciable rate under these conditions. Above 120°C. oxidative scission should be rapid and not entirely dependent on shear. However, even if

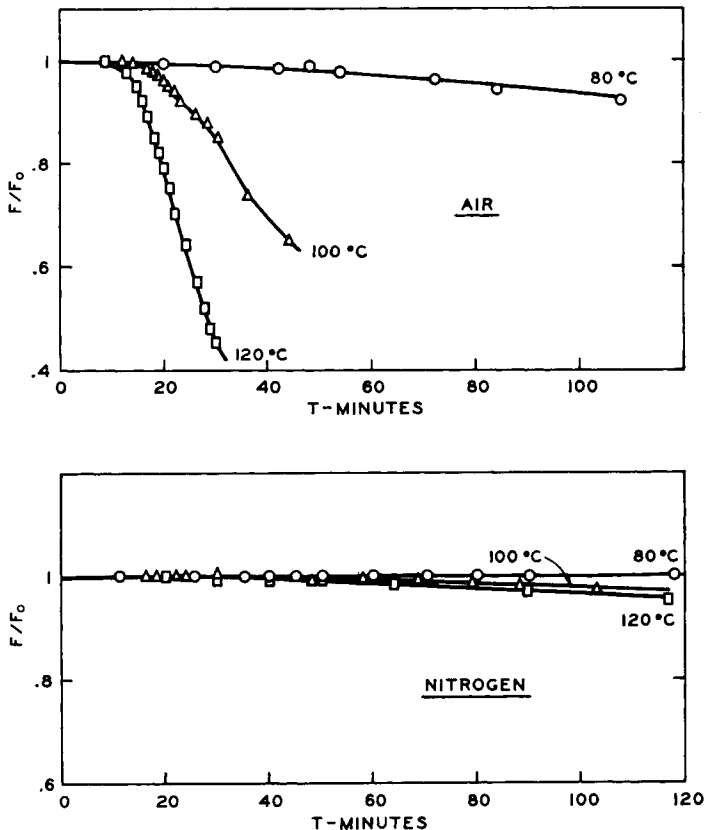


Fig. 3. Stress relaxation of crosslinked *cis*-polybutadiene. (F = stress at time T ; F_0 = original stress.)

shear contributes only little to the overall breakdown rate, the mixing action associated with it exposes new surface to oxygen and undoubtedly becomes an important contributing factor in hot oxidative mastication. These predictions are amply borne out by experiment. Figure 4 shows that polymer masticated cool (60°C. jacket temperature) undergoes no breakdown in air. A small amount of toughening is indicated by the constancy of the torque at rising temperature, but this is a minor effect. (It is a peculiarity of the mixing action of *cis*-polybutadiene in the Plastograph at high speeds that the torque is remarkably insensitive to temperature.) The results at 140°C. jacket temperature clearly demonstrate breakdown. At the end of this run the inherent viscosity had dropped to 1.97, the polymer contained no gel, and the low shear extrusion had fallen to 2.3 mg./min. The latter result is the consequence of the recombination reactions leading to branched and crosslinked structures. By carrying mastication to longer times this trend can be reversed, the reduction in molecular weight overcoming the effect of branching on the low shear viscosity.

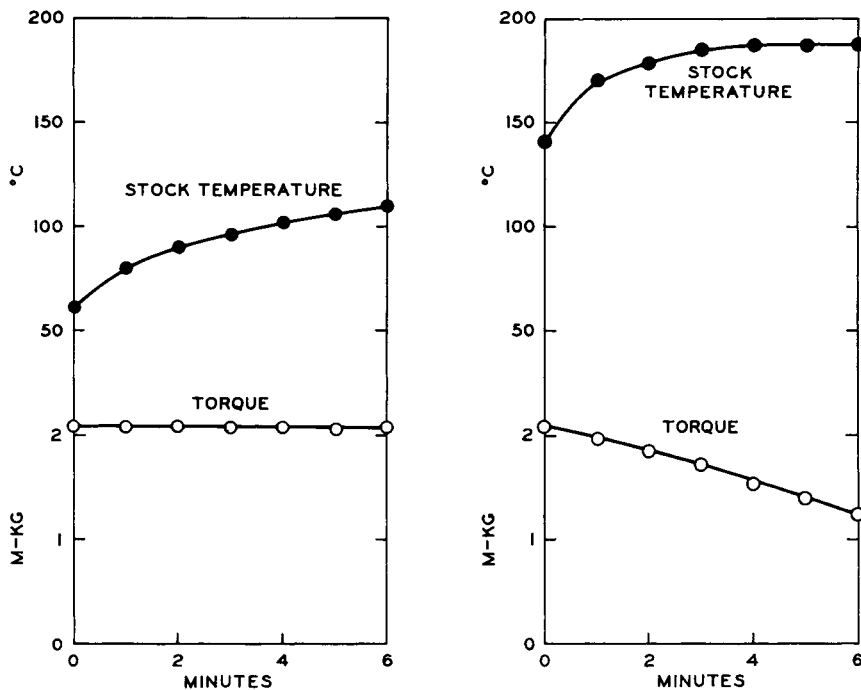


Fig. 4. Mastication of *cis*-polybutadiene in air at 60 and 140°C. jacket temperature.

Action of Chemical Plasticizers

Further evidence for the relative unimportance of the shear-initiated scission of *cis*-polybutadiene at any temperature is derived from the behavior of chemical plasticizers ("peptizers"). In cold mastication of *cis*-polybutadiene no effect would be expected, since no appreciable scission occurs. In anaerobic hot mastication resulting in thermal scission augmented by shear, an effect might be observed if the mechanism of chemical plasticization involved direct reaction of the plasticizer with the hydrocarbon radicals. This mechanism appears quite unimportant in *cis*-polybutadiene; the action of chemical plasticizers is almost entirely dependent on initiation by oxygen. This may again be demonstrated by two types of measurements. Figure 5 shows mastication experiments in presence and absence of 0.5% of phenylhydrazine. No increase in plasticity results from the peptizer in absence of oxygen. Another clue to the situation is obtained from stress relaxation of vulcanizates containing peptizers. If reaction with shear-generated hydrocarbon chain radicals were the mechanism of chemical plasticization, the effect on continuous stress relaxation would be nil, since the peptizer does not initiate scission. Experiments, however, show that the oxidative scission rate is increased, leading to more rapid stress relaxation. Figure 6 illustrates this with vulcanizates impregnated with zinc pentachlorothiophenol/iron phthalocyanine (Endor-

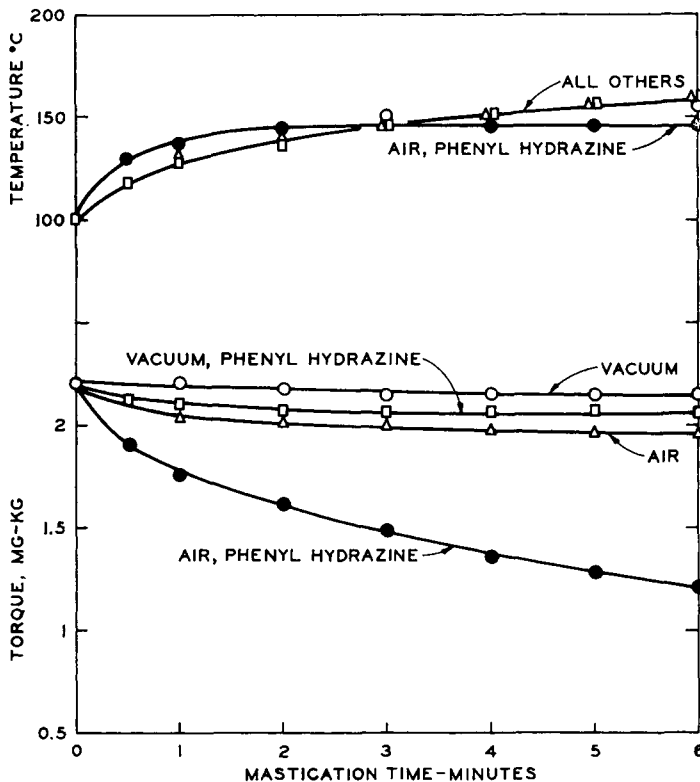


Fig. 5. Plastograph breakdown curves of *cis*-polybutadiene containing 0.5 phr phenylhydrazine (100 rpm).

E. I. du Pont). A mechanism of chemical plasticizer action based on oxidative initiation of scission has been proposed by Furukawa.¹¹ The present results show that in *cis*-polybutadiene a mechanism of this type is dominant. A number of compounds useful in the promotion of oxidative scission have been found; unfortunately present knowledge of oxidation mechanisms in diene polymers does not permit any *a priori* predictions about specific compounds, nor does it allow ready generalizations to be made regarding classes of compounds.

Effect of Antioxidants

In view of the oxidative nature of the scission reaction during hot mastication, one might expect antioxidants to exert some significant retarding effects. In general, this does not appear to be true (Table III); the effect of antioxidants is found to be surprisingly small.

Effect of Carbon Black

Carbon blacks appear to exert only secondary effects on the breakdown of *cis*-polybutadiene or the action of chemical plasticizers, and trends

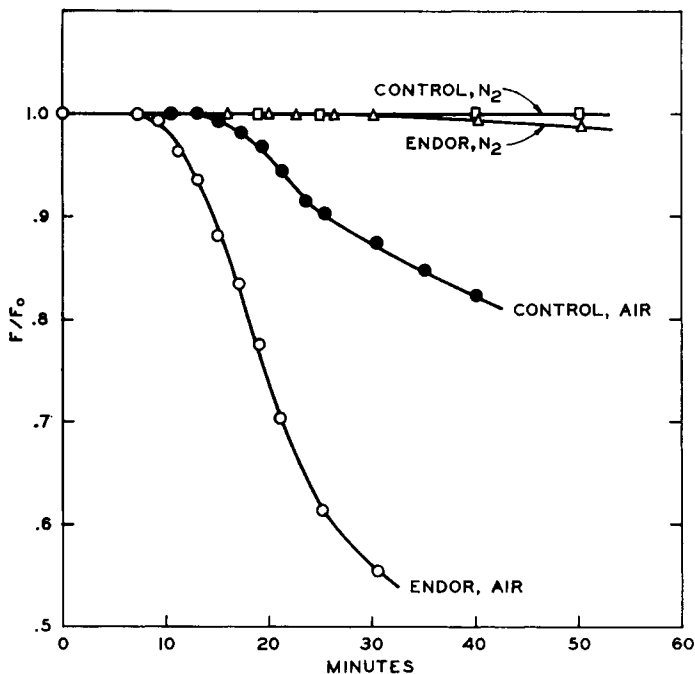


Fig. 6. Stress relaxation at 100°C. of *cis*-polybutadiene networks in presence and absence of a peptizer.

observed in mastication of the gum remain preserved in black stocks. The quantitative interpretation of mastication data is, of course, complicated by questions of dispersion and carbon gel formation, but clear evidence for scission is obtained from increases in plasticity on hot mastication in the presence of air, either alone or with certain oxidation catalysts. A representative example is shown in Figure 7.

TABLE III
Effect of Some Antioxidants during Hot Mastication for 6 Minutes

Antioxidant	Anti-oxidant concn., %	Atmosphere	Rotor speed, rpm	Jacket temp., °C.	Final temp., °C.	Final torque, m.-kg.
None	—	Air	100	140	171	1.37
A.O.2246	0.5	Air	100	140	174	1.44
Polygard	0.5	Air	100	140	170	1.29
Phenyl- α -naphthylamine	0.5	Air	100	140	173	1.38
Ionol	0.5	Air	100	140	172	1.36

Role of Molecular Weight Distribution

It was shown above that shear-initiated scission is not an important reaction in the mastication of typical *cis*-polybutadienes, and we have indicated

this result to be in essential harmony with theory provided the molecular weight of the molecules undergoing scission is of the order of 10^5 . The molecular weight distribution of *cis*-polybutadiene is such that it lacks the very high molecular weight fractions common in emulsion polymers¹⁰ or natural rubber. When such fractions are supplied shear breakdown at low temperatures may be caused to occur as would be predicted by the Bueche theory of mastication.

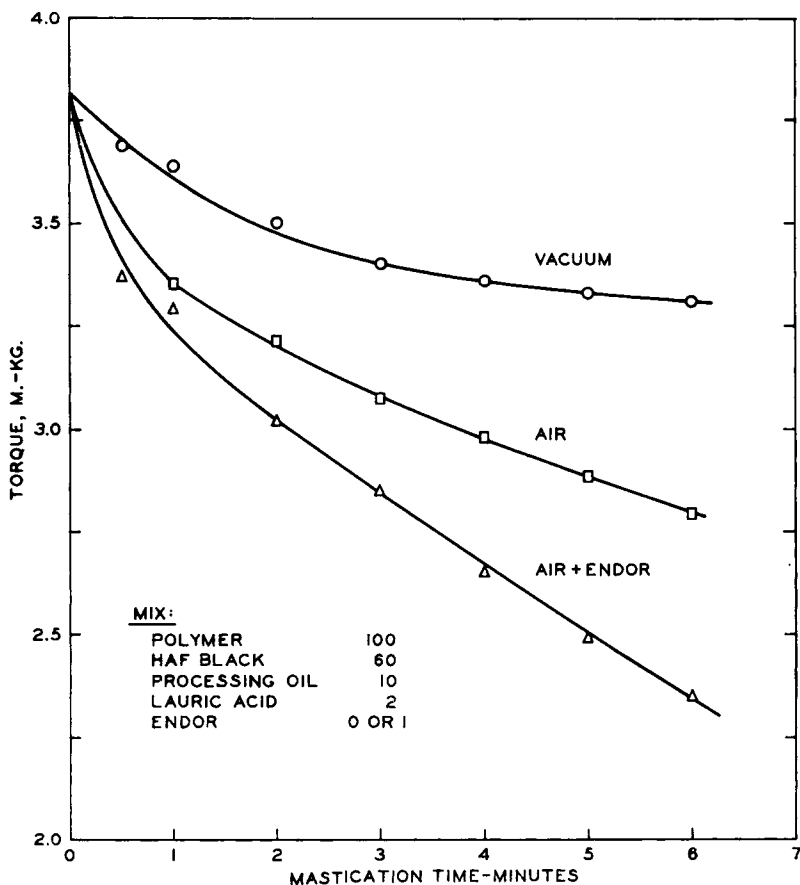


Fig. 7. Mastication of *cis*-polybutadiene in presence of carbon black (150 rpm, 65°C. jacket temperature).

We have estimated above that for a conventional *cis*-polybutadiene $F_0\delta$ might be of the order of 1000 cal./mole at 430°K. where evidence of shear degradation is barely detectable, and $E = 40,000$ cal./mole. Whether shear-initiated scission will occur in a polymer will depend on the temperature (for purpose of demonstration to be chosen well below the threshold for oxidative scission) and the value of $F_0\delta$. By comparison with the above

example, making use of eq. (2), we estimate that shear breakdown will occur at an appreciable rate if

$$(T/F_0\delta)^{1/2}e^{-43000-F_0\delta/RT} \gg (430/1000)^{1/2}e^{-3300/860}$$

At 300°K. this will require a shear energy $F_0\delta$ of about 14,000 cal./mole or more. Equation (3) shows that in a rubber consisting of a small fraction of very high molecular weight material, M , in a medium of low molecular weight polymer, F_0 (for the high molecular weight molecules added) will be proportional to M^2 . It is also proportional to the viscosity and rate of shear. By supplying a fraction twice the molecular weight of the highest fraction already present we increase F_0 for the longest molecules by a factor of 4. The remaining increase in shear energy over our original example at 430°K. is readily supplied by the increase in viscosity with decreasing temperature.

TABLE IV
Response of Standard and Bimodal Distribution Polymers to Mastication in Air

Polymer	Stock temperature range, °C. ^a	Mixing time, min.	Torque at 100 rpm, m.-kg.		Inherent viscosity		Gel	
			Initial	Final	Initial	Final	Initial	Final
Standard	25-105	10	2.02	2.04	2.51	2.51	0	0
	140-171	9	2.00	1.24	2.51	1.85	0	0
Bimodal	25-115	10	2.85	1.90	3.95	3.84	0	0
	25 ^b	25	—	—	3.95	3.19	0	0
	140-173	4	1.75	2.13	3.95	3.30	0	0
	140-183	20	1.71	1.14	3.95	1.00	0	20

^a Jacket (initial) temperature to maximum or dump temperature.

^b Masticated on 2-in. roll mill, 20 mil gap, 18 rpm, friction ratio 1.2:1.

To test this prediction a bimodal distribution polymer was prepared containing 16.4% of a fraction of inherent viscosity of 10.5, the whole polymer having an inherent viscosity of 3.95. This rubber was compared to a standard polymer in both hot and cold mastication in air. The results are shown in Table IV. All but one of these experiments were carried out in the Plastograph. The results show clearly that both rubbers broke down smoothly during hot mastication, but only the bimodal distribution polymer gave any evidence of breakdown on cold mixing. The torque readings for the bimodal polymer appear contradictory to the inherent viscosity data. This has been found to be the result of increased thermoplasticity of such polymers.* The increase in torque at 4 min. mixing time during hot mastication, coupled with clear evidence of breakdown, stems

* The increased thermoplasticity of the bimodal distribution polymer may be apparent rather than real. Because of the complex geometry of the mixing head, speed-torque-temperature relations in the Brabender Plastograph do not always follow the simple relationships expected from activation energies for viscous flow.

from the fact that the polymer is no longer bimodal at this point. This is demonstrated in the following paragraphs.

To illustrate the changes in molecular weight distribution caused by mastication, approximate distributions in sedimentation coefficients were

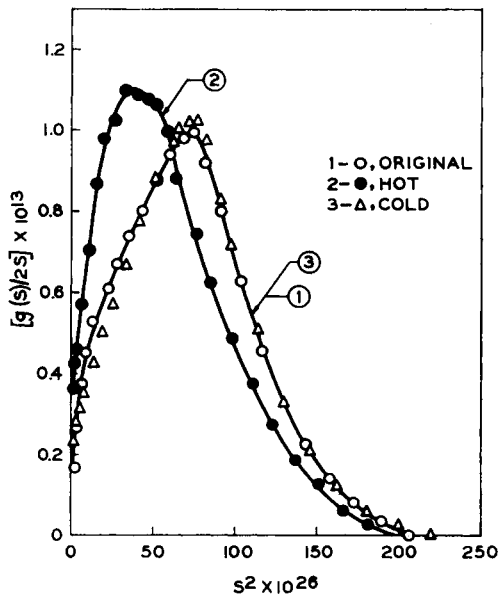


Fig. 8. Effect of mastication on molecular weight distribution of a conventional *cis*-polybutadiene.

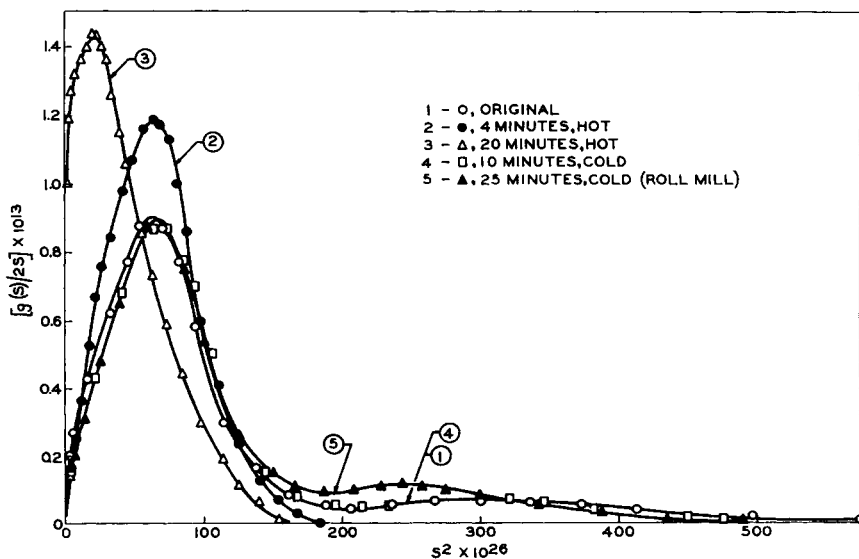


Fig. 9. Effect of mastication on molecular weight distribution of bimodally distributed *cis*-polybutadiene.

determined using a Spinco ultracentrifuge. Since the sedimentation coefficient, s , is proportional to M^n , where $n \sim 1/2$, the distribution in its square will be similar to that in M .

Figures 8 and 9 show the distributions in s^2 for the polymers of Table IV. For the conventional polymer, within experimental error, no change in the distribution is evident on cold mastication. Breakdown is clearly demonstrated for hot mastication. In the example of the bimodal polymer we note that the high molecular peak is still present after cold mastication. For the 10-min. mix in the Plastograph no change from the original distribution is evident, confirming the insignificant change indicated by the inherent viscosity result. However, in the roll-milled polymer we note a definite change in the high molecular peak. The amount of polymer in excess of $s^2 = 330 \times 10^{-26}$ has been diminished, while polymer ranging in s^2 between 120 and 330×10^{-26} is now present in larger quantity. The main peak in the molecular weight distribution is unaffected. This behavior is exactly as required by the theory of shear degradation. The concentration of stress near the center of the molecules would lead one to expect scission products at about half the value of the original molecular weight of the molecules cleaved.^{2,6} Thus original molecules of s^2 between 300 and 600×10^{-26} should appear between 150 and 300×10^{-26} in the masticated polymer.

Hot mastication of bimodal polymer is seen to occur in two almost distinct stages. The high molecular tail is removed very quickly, being entirely absent in the 4-min. sample. This is followed by general breakdown. The preferential attack on the longest molecules follows from obvious statistical considerations.

In conclusion, we again note the small role played by shear initiation of scission in the cold mastication of *cis*-polybutadiene. Even though introduction of very high molecular weight material allows the effect to be demonstrated, its magnitude is surprisingly small.

Processability of Conventional Stocks

We have demonstrated that hot mastication in presence of oxygen represents a feasible means of reducing the primary molecular weight of *cis*-polybutadienes. This breakdown is accelerated by oxidation catalysts and occurs in both gum and black stocks. The masticated rubber has both a lower molecular weight and, because of the accompanying crosslinking reactions, inevitably becomes branched. Both factors should lead to improved processability.

Table V shows some typical results comparing stocks processed by hot mastication, with and without the use of chemical plasticizers. Polymer, black and chemicals, except antioxidant and curatives, were mixed in a B-Banbury at 118 rpm for 7 min. Curatives and antioxidant were added on a re-mill. The results show clearly the beneficial effects of the breakdown catalysts. In all cases plasticity is increased and extrusion appearance and mill handling are improved. Vulcanizate properties are altered somewhat. Oxidative mastication leads to higher modulus, lower

TABLE V
Processing of a 100% *cis*-Polybutadiene Compound with and without
Chemical Plasticizers

	Chemical plasticizer			
	None	RPA #6, 2 phr	Phenyl- hydrazine, 0.5 phr	Fe stearate 0.5 phr; cumene hydro- peroxide 0.15 phr
Mixing Cycle				
Max. power, kw.	10.0	10.3	10.5	9.8
Time to max. power, min.	4	3	3	3.5
Power at dump, kw.	10.0	9.0	7.5	8.8
Dump temperature (7 min.), °F.	310	330	330	320
Processing Properties				
Compounded Mooney (MS-1 ¹ / ₂ , 212 °F.)	43	34	33	38
Extrusion rate at 250°F., g/min.	117.5	108.5	100.5	96.5
Extrudate appearance, Garvey die rating	9+	12	12-	11
Mill banding at 158°F.	Loose	Sl. loose	Tight	Loose
Surface appearance	Rough	Sl. rough	Smooth, glossy	Sl. rough, glossy
Overall mill rating	2	4	9	6
Vulcanizate properties ^a				
v_r ^b	0.405	0.417	0.408	0.409
300% Modulus, psi	1470	1790	1710	1550
Tensile strength, psi	2620	2530	2400	2430
Elongation, %	450	370	370	410
Resilience (Yerzley), %	71.9	75.8	75.7	74.1
Heat build-up, °F.	56.5	48.7	50.0	51.7
Shore A hardness	64	62.5	62	63

^a Recipe as shown in Experimental Section; with sulfur 1.75 phr; NOBS Special 1.0 phr.

^b Inverse equilibrium swelling ratio in *n*-heptane, a measure of cure.

tensile strength (due to reduction in primary molecular weight) and, somewhat surprisingly, lower hysteresis.

The employment of oxidation catalysts to promote breakdown in processing would appear to entail some risk with regard to the stability of the finished vulcanizates. This problem has been studied in some detail. While it is quite easy to detect residual action of peptizers by measurements of oxidative stress relaxation on the vulcanizates, the chain scission occurring during aging is fully compensated by crosslinking.

Figure 10 shows oxidative stress relaxation curves for vulcanizates prepared under nonoxidative and oxidative mixing conditions. The former were compounded on a cool roll mill, the latter were masticated hot (in air,

TABLE VI
Effect of Mastication on Vulcanizate Aging^a

Properties	Nonoxidative mixing; no peptizer		Oxidative mixing; no peptizer		Oxidative mixing; Fe stearate/CHP (0.5/0.15)		Oxidative mixing; phenylhydrazine (0.5)	
	Orig.	Aged ^b	Orig.	Aged ^b	Orig.	Aged ^b	Orig.	Aged ^b
<i>v_r</i> ^c	0.411	0.449	0.403	0.450	0.413	0.444	0.401	0.439
300% Modulus, psi	1590	—	1480	—	1770	—	1880	—
Tensile strength, psi	2390	1780	2210	1870	2760	2490	2570	2100
Elongation, %	420	220	410	250	430	270	380	240
Resilience, %	71	75	72	78	77	81	78	82
Heat build-up, °F.	62	58	58	49	49	47	48	41

^a Recipe as shown in Experimental section with sulfur 1.6 phr; Santocure 1.0 phr.

^b Aged 24 hr. at 212°F. in air oven.

^c Inverse swelling ratio in *n*-heptane.

dump temperature 163°C.) in the Plastograph. The increase in scission rate due to residual peptizer action is quite apparent. Physical properties of the vulcanizates before and after accelerated aging, however, show the loss in tensile strength and elongation to be no more severe than in polymer

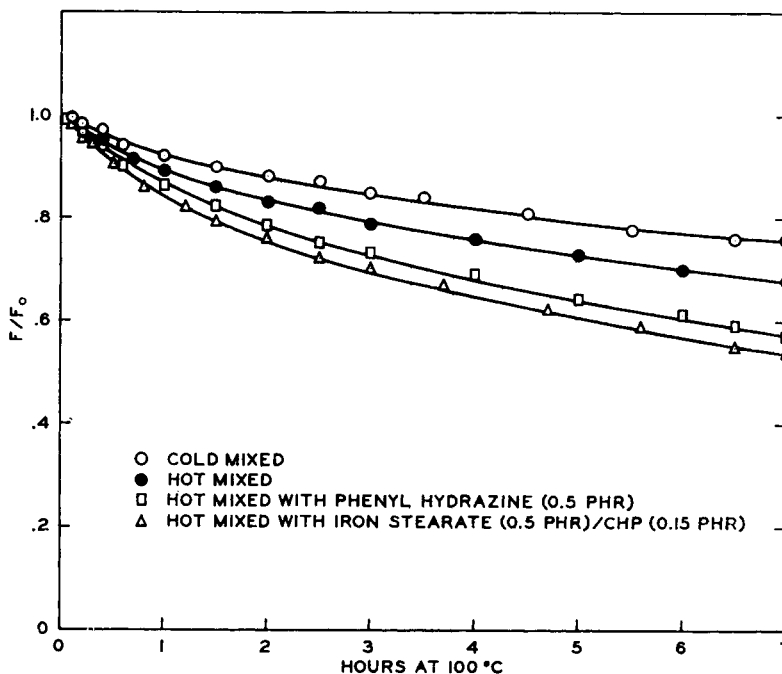


Fig. 10. Effect of oxidative mastication on chain scission in finished vulcanizates, determined by stress relaxation in air, 100°C., 50% elongation.

compounded nonoxidatively (Table VI). The equilibrium swelling data show that the rubber undergoes net crosslinking on aging in all examples. This results in lowered hysteresis of the aged vulcanizates.

V. CONCLUSIONS

Conventional *cis*-polybutadiene does not undergo breakdown by shear-induced scission at temperatures below 120°C. Above this temperature the polymer may be broken down by oxidative scission.

By supplying fractions of very high molecular weight, polymers subject to shear degradation during cold milling may be prepared.

Chemical plasticizers are effective in high temperature oxidative mastication of *cis*-polybutadienes. They are ineffective in hot mastication in the absence of oxygen.

Cis-polybutadiene compounds subjected to hot oxidative mastication display improved processing characteristics. When oxidation catalysts are

used to accelerate breakdown, some residual action of the chemical plasticizers is detectable in the finished vulcanizates by stress relaxation measurements. However, network scission is compensated by crosslinking, and no serious loss in vulcanizate properties results.

References

1. Railsback, H. E., *Proc. Intern. Rubber Conf., 3rd Conf., Washington, D. C.*, November 1959.
2. Scanlan, J., and W. F. Watson, *Rubber Chem. Technol.*, **33**, 1201 (1960).
3. Pike, M., and W. F. Watson, *J. Polymer Sci.*, **9**, 229 (1952).
4. Mullins, L., and W. F. Watson, *J. Appl. Polymer Sci.*, **1**, 245 (1959).
5. Angier, D. J., W. T. Chambers, and W. F. Watson, *J. Polymer Sci.*, **25**, 129 (1957).
6. Bueche, F., *J. Appl. Polymer Sci.*, **4**, 101 (1960).
7. Bristow, G. M., *Trans. Inst. Rubber Ind.*, **38**, T29, T104 (1962).
8. Tobolsky, A. V., and A. Mercurio, *J. Am. Chem. Soc.*, **81**, 5535, 5539 (1959).
9. Railsback, H. E., W. T. Cooper, and N. A. Stumpe, *Rubber Plastics Age*, **39**, 867 (1958).
10. Short, J. N., G. Kraus, and R. P. Zelinski, *Rev. Gen. Caoutchouc*, **40**, 253 (1963).
11. Furukawa, J., and S. Yamashita, *Mem. Fac. Eng. Univ. Kyoto*, **23**, 111 (1961); *J. Soc. Rubber Ind. Japan*, **30**, 584 (1957).

Résumé

La mastication à froid du caoutchouc naturel en présence d'oxygène conduit à une scission par un mécanisme de rupture ayant pour conséquence une stabilisation des radicaux libres par l'oxygène tandis qu'à température plus élevée la scission oxydante devient le mécanisme prédominant. Les études du comportement du *cis*-polybutadiène montrent que des réactions similaires se produisent, mais à vitesse plus réduite. La dégradation par rupture est particulièrement difficile à démontrer dans le cas des *cis*-polybutadiènes typiques. Ceci est mis en rapport avec la distribution des poids moléculaires de ces polymères dans lequel le plus souvent les espèces à poids moléculaires élevés font défaut, espèces les plus sensibles à des dégradations par cisaillement en accord avec la théorie de F. Bueche. On a montré que lors de l'addition de fractions à poids moléculaire élevé, des ruptures peuvent se produire. Tous les *cis*-polybutadiènes subissent une rupture oxydante à haute température; la vitesse de scission devient appréciable à 140°C. On a trouvé un certain nombre de catalyseurs d'oxydation qui augmentent particulièrement la vitesse de scission, sans conduire à une grande augmentation du pontage. Des améliorations importantes dans les processus de fabrication peuvent être réalisées de cette manière.

Zusammenfassung

Kalte Mastizierung von Naturkautschuk in Anwesenheit von Sauerstoff führt durch einen Scherungsmechanismus zur Spaltung mit nachfolgender Stabilisierung der freien Radikale durch Sauerstoff, bei hohen Temperaturen hingegen wird die oxydative Spaltung zum vorherrschenden Mechanismus. Untersuchungen des Verhaltens von *cis*-Polybutadien zeigen, dass ähnliche Reaktionen zwar wirksam sind, aber mit weit geringerer Geschwindigkeit verlaufen. Bei typischen *cis*-Polybutadienen ist der Scherungsabbau besonders schwierig zu erreichen. Dies hängt mit der Molekulargewichtsverteilung in diesen Polymeren zusammen, denen meistens die sehr hochmolekulare am meisten durch scherungsbedingten Abbau angreifbare Komponente mangelt, übereinstimmend mit der Theorie von F. Bueche. Man kann bei Hinzufügen einer solcher

hochmolekularen Fraktion einen Scherungsabbau beobachten. Alle *cis*-Polybutadiene zeigen oxydativen Abbau bei hohen Temperaturen; die Spaltungsgeschwindigkeit wird über 140°C merklich. Man fand eine Anzahl von Oxydationskatalysatoren, die die Spaltungsgeschwindigkeit wesentlich vergrössern, ohne zu einem entsprechenden Anwachsen der Vernetzung zu führen. Bemerkenswerte Verbesserungen der Verarbeitung können dadurch verwirklicht werden.

Received September 23, 1963