

## Mastication. IX. Shear-Dependence of Degradation on Hot Mastication

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The rate of degradation of rubber during mastication is minimal at about 115°C., degradation increasing progressively on lowering or raising the temperature as far below or above this temperature as practicable.<sup>1</sup> Designation of the degradation processes with the negative and positive temperature coefficients as "cold" and "hot mastication," respectively, is supported by differences in their chemical mechanisms. The essential degradation step of cold mastication is rupture of rubber molecules by the imposed deforming forces to radicals which are converted to the degraded molecules after reaction with oxygen or other radical acceptor present in the rubber.<sup>2,3</sup> Hot mastication is less well understood; scission appears to be by an oxidative reaction,<sup>2,4</sup> with the implication that mastication serves in the main to expose fresh surfaces for absorption of oxygen.

The mechanicodegradation of cold mastication produces an unusually rapid decrease in viscosity with molecular weight, logarithmic plotting of these two quantities giving an apparent  $\alpha$ , according to the relation  $[\eta] = KM^\alpha$ , of greater than unity.<sup>5</sup> The value of  $\alpha$  for fractionated rubber<sup>6</sup> is 0.67. The apparent high  $\alpha$  is most readily explicable by a decrease in  $K$  on degradation, while  $\alpha$  has its normal value of 0.67 for natural rubber. A decrease in  $K$  would occur if the molecular weight distribution around the mean became sharper. This distribution change has been considered to be caused by rupture only of molecules above a certain molecular weight, and this in the central sections of the molecules.<sup>5</sup>

For the oxidation of thin films and latex or any other chemical process whereby scission conceivably occurs with equal probability at every monomeric unit, the chain-length distribution would tend to a random one. In particular, if the rubber had initially a random distribution, viscosity-molecular weight decrease would yield an

$\alpha$  equal to that for fractionated rubber and a  $K$  which is  $\Gamma(\alpha + 2)$  times higher.<sup>7</sup>

Viscosity-molecular weight data on hot mastication have not been previously published. If a normal chemical degradation takes place, a difference in the viscosity-molecular weight relationship from that on cold mastication should be detectable. Differences in molecular weight distribution should also be reflected in differences in other properties of masticated rubber and, to a lesser extent, of vulcanized products.

A comparison of viscosity-molecular weight relationships and other properties of rubbers masticated in air forms a starting point for answering the complex query of the relative merits of cold and hot mastication. Interaction of rubber with fillers<sup>8</sup> and vulcanizing ingredients would then have to be systematically investigated.

### EXPERIMENTAL MATERIALS AND METHODS

**Rubber.** A 15-lb. smoked sheet of yellow-circle grade was homogenized on a twin-roll mill at 100°C. to provide a stock supply of rubber. Its molecular weight and limiting viscosity were 283,000  $\pm$  38,000 and 444 g.<sup>-1</sup> ml., respectively.

**Rubber Degradation.** A laboratory-size B Banbury mixer and a small uni-rotor mixer<sup>9</sup> were employed. No differences were detected in rubber samples masticated to the same extent of breakdown by the two machines. The Banbury mixer was charged with 400 g. rubber and operated for chosen times with cooling water at 11°C. or steam at 40 lb./sq. in. to keep the rubber within 5°C. of 55°C. and 140°C., respectively, after the first 5 min. of mastication. The uni-rotor mixer with the twisted blade rotor fitted<sup>9</sup> maintained the charge of 6 g. rubber to within 2°C. of the temperature of the liquid in which the assembly was immersed.

Rubber was also degraded without mastication in films of thickness selected in the range 0.1–0.5 mm. Successive portions of a 2% benzene solution were dried down by warming in a  $10 \times 10 \times 0.5$  glass or metal boat floating on mercury and under a flow of nitrogen. The boat with the dried film was then floated on Wood's metal in a box immersed in a paraffin oil bath.

**Viscosities.** Limiting viscosity numbers were determined from flow times of solutions in Ubbelohde viscometers at three concentrations from 0.04–0.15 g. rubber/100 ml. benzene. Viscosities of rubber containing vulcanizing ingredients were measured after centrifuging for 20 min. at 20,000 g. to give clear solutions.

Viscosities of the bulk rubber at 100°C. were measured by standard methods with Mooney and Wallace Rapid Plastimeters<sup>10</sup> and are given in Wallace viscosity units,  $\eta_M$  and  $\eta_W$ , respectively.

**Osmotic Molecular Weights.** Osmotic pressures were recorded for four solutions of each sample over the range 0.15–1.2 g. rubber/100 ml. benzene after these were permitted to stand for two days in four Zimm-Meyerson osmometers fitted with Ultracella Feinst membranes.<sup>11</sup> The best  $\pi/c$  versus  $c$  straight line was derived by least squares, with limits on the molecular weight from the extrapolated osmotic pressure given by the average deviation of the measured  $\pi/c$  values from the best straight-line plot.

**Crosslinking.** Crosslinking agents, 3 parts di-

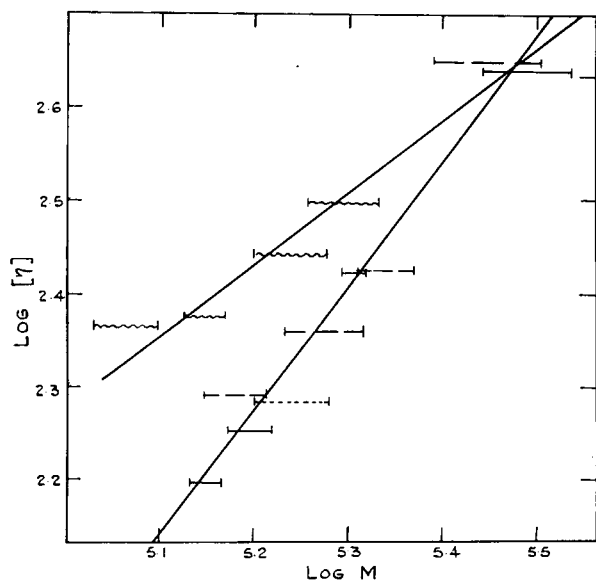


Fig. 1. Viscosity-molecular weight data for rubbers after degradation in thin films ( $|\sim\sim\sim|$ ) and on mastication at 55 (—), 120 (---), and 140°C. (- - -).

cumyl peroxide per 100 parts rubber or the recipe: 5 zinc oxide, 1 stearic acid, 1 phenyl- $\beta$ -naphthylamine, 0.7 *N*-cyclohexenyl-2-benzthiazyl sulfenamide (Santocure of Monsanto Ltd), 3 sulfur were incorporated on twin rolls at 100°C. and the compounded rubber rested overnight. Crosslinked sheets,  $3.5 \times 3.5 \times .075$  in., were prepared by heating in a rubber mold at 140°C. for 50 and 30 min., respectively, with the peroxide and sulfur recipes. The rubbers were then acetone-extracted and dried.

Swellings in *n*-decane at 25°C. are reported as the volume fraction of rubber in the swollen gel,  $v_r$ , allowance being made for nonrubber constituents in the gel. The elastic constants of the rubber,  $C_1$  and  $C_2$ , were evaluated from stress-strain data obtained by hanging increasing weights,  $f$ , on  $10 \times 0.45$ -cm. strips cut from the vulcanized sheets and measuring the extension ratio,  $\lambda = l/l_0$ , 3 min. after each loading.<sup>12</sup>

## RESULTS

**Masticated Rubbers.** The measurements made on rubber batches masticated in the Banbury mixer are recorded in Table I. The uncertainty in the

TABLE I  
Data on Rubber Samples after Cold and Hot Mastication

Masti- cation, temp., °C.	Masti- cation, min.	Mol. wt. $\times 10^3$	$[\eta]$ , g. <sup>-1</sup> ml.	Mooney viscosity	Wallace vis- cosity
55	5	298	434	66	44
55	15	202	264	37	27
55	30	158	179	16	14
55	45	142	157	10.5	11
140	5	283	444	66	42
140	15	220	293	40	27
140	30	192	228	24	19
140	45	153	195	16.5	14

osmotic molecular weights, shown graphically in Figure 1, being taken into account, the limiting viscosity number-molecular weight relationship obtained for hot-masticated samples is the same as that for cold-masticated samples and is expressed by

$$[\eta] = 2.29 \times 10^{-7} M^{1.33} \quad (1)$$

This is somewhat different from that previously found for a more porous denitrated cellulose membrane with a Fuoss and Mead osmometer,<sup>5</sup> the latter giving results higher by 10,000 and 60,000 for molecular weights of the order of 100,000 and 250,000, respectively. The present results

TABLE II. Viscosities of Oxidized Rubber Films

Min. at 140°C.	Film thickness, mm.	Glass or steel boat	$[\eta]$ , g. <sup>-1</sup> ml.	Min. at 140°C.	Film thickness, mm.	Glass or steel boat	$[\eta]$ , g. <sup>-1</sup> ml.
0	—	—	580	110	.15	S	238
20	.15	G	400	110	.45	S	267
	.15	S	471	110	.6	G	274
50	.15	S	413	170	.15	G	200
	.45	S	460	170	.3	G	203
	.3	G	315	170	.15	S	162
	.15	S	348	170	.45	S	216
	.6	G	356	170	.6	G	232
	.6	G	404	170	.6	G	226
80	.15	G	315	0 (at 130°C.)	—	—	576
	.15	S	315	60 (at 130°C.)	.15	S	456
	.6	G	321	180 (at 130°C.)	.15	S	318
	.45	S	327	240 (at 130°C.)	.15	S	254
110	.3	G	231	300 (at 130°C.)	.15	S	256

TABLE III. Viscosities of Masticated Rubber

Min.	Temp., °C.	Rotor speed, rpm	$[\eta]$ , g. <sup>-1</sup> ml.	Min.	Temp., °C.	Rotor speed, rpm	$[\eta]$ , g. <sup>-1</sup> ml.
0	140	46	510	30	140	245	153
10	140	46	392	40	140	245	129
20	140	46	323	0	130	46	570
30	140	46	277	10	130	46	406
40	140	46	343	20	130	46	358
50	140	46	210	60	130	46	261
0	140	245	510	90	130	46	206
10	140	245	225	120	130	46	180
20	140	245	173				

TABLE IV. Physical Properties of Vulcanizates after Cold and Hot Mastication

Mastication, temp., °C.	Mastication, min.	(Mol. wt.) <sup>-1</sup> × 10 <sup>6</sup>	Vulcanizing recipe	$C_1$	$C_2$	$C_{1\infty}$	$M_c$	$\lambda^*$	$\nu_r$
				dynes/cm. <sup>2</sup> × 10 <sup>6</sup>					
55	5	3.95	Peroxide	1.37	.96	1.59	7170	2.65	.271
55	15	5.43	"	1.34	.93	1.67	6820	2.7	.273
55	30	6.45	"	1.22	.84	1.63	7000	2.7	.265
55	45	7.14	"	1.18	.83	1.64	6950	2.7	.265
140	5	4.40	"	1.53	.91	1.78	6400	2.5	.185
140	15	5.21	"	1.55	.91	1.86	6130	2.5	.288
140	30	5.68	"	1.51	.92	1.86	6130	2.5	.287
140	45	6.21	"	1.49	.87	1.88	6060	2.5	.289
55	5	4.22	Sulfur	2.04	1.23	2.28	5440	2.35	.321
55	15	5.81	"	2.04	1.20	2.32	5340	2.3	.318
55	30	6.62	"	2.01	1.14	2.34	5290	2.3	.318
140	5	4.15	"	1.89	1.26	2.12	5850	2.4	.317
140	15	4.89	"	1.87	1.25	2.15	5770	3.45	.323
140	30	5.49	"	1.87	1.12	2.20	5640	2.5	.312
140	45	6.25	"	1.83	1.13	2.20	5590	2.5	.310

enhance the qualitative conclusions previously drawn<sup>5</sup> and are preferred in view of the tests of absolute reliability carried out with the membranes used.<sup>11</sup>

The relations between  $[\eta]$ ,  $\eta_M$ , and  $\eta_W$  are likewise the same for hot- and cold-masticated rubbers. These are given by:

$$\eta_W = 5 + 0.58\eta_M \quad (2)$$

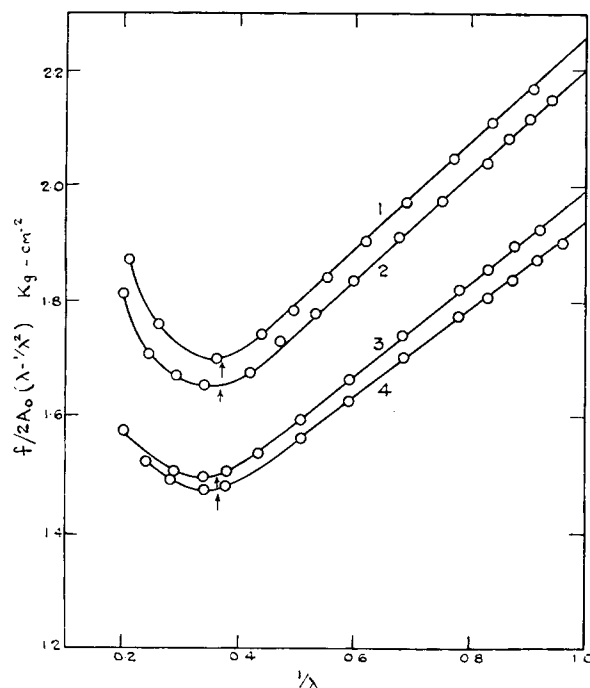


Fig. 2. Simple extension stress-strain results on peroxide vulcanizates prepared from rubbers masticated at 55°C. for (1) 5, (2) 15, (3) 20, and (4) 45 min.

$$[\eta] = 60 + 8.7\eta_w \quad (3)$$

and

$$[\eta] = 104 + 5.0\eta_M \quad (4)$$

**Oxidized Films.** The viscosity-molecular weight data obtained with films 0.2 mm. thick after heating in air at 140°C. for periods up to 3 hr. are given in Figure 1. The relation between the two measurements is markedly different from that for masticated rubbers. From the best straight line through the results, the relationship is:

$$[\eta] = 2.67 \times 10^{-4} M^{0.77} \quad (5)$$

**Rates.** The rates of degradation of cast films were not closely reproducible (Table II), but were sufficiently so to permit differentiation of the rate from that on mastication at the same temperature. The variations in rate were clearly not attributable to film thickness or the nature of the surface on which the film was cast. Degradation on mastication was more reproducible; the viscosities for each series recorded in Table III at constant temperature and rotor speed were for two batches of rubber being masticated, small samples being removed for measurement.

**Properties of Vulcanizates.** Stress-strain measurements were analyzed by plotting  $f/2A_0[\lambda - (1/\lambda^2)]$  against  $1/\lambda$  and were characterized as to the intercept, slope, and departure of this plot

from linearity by the elastic constants.  $C_1$  and  $C_2$  and the quantity  $\lambda^*$  "lambda upturn," respectively.<sup>12</sup> A typical set of data obtained on peroxide vulcanizates after mastication at 55°C. is shown in Figure 2. The value of  $\lambda^*$  was selected as that value of  $\lambda$  at which  $f/2A_0[\lambda - (1/\lambda^2)]$  departed from the linear plot by the arbitrary significant amount of  $2^{1/2}\%$  of  $C_1$ .

The results for hot- and cold-masticated rubbers are reported in Table IV. Also included are  $C_1$  data corrected to initial infinite molecular weight,  $C_{7\infty}$ , and molecular weight between cross links,  $M_c$ , from  $C_{7\infty} = \rho RT/2M_7$ , where  $\rho = 0.91$  is the density of rubber.

## DISCUSSION

**Masticated Rubber.** Contrary to the viscosity-molecular weight relationship predicted for a random scission reaction, rubber samples after hot mastication followed closely the relationship obtained with cold-masticated rubber (Fig. 1). Hot-masticated samples clearly differed in this respect from oxidized rubber films, which gave a value of the exponent  $\alpha$  expected for a random scission reaction. These observations suggest that hot as well as cold mastication is a shear-dependent process.

A prediction from this conclusion is a more rapid degradation on hot mastication than on static oxidative aging. This prediction is borne out by the rates of bond scission shown in Figure 3,

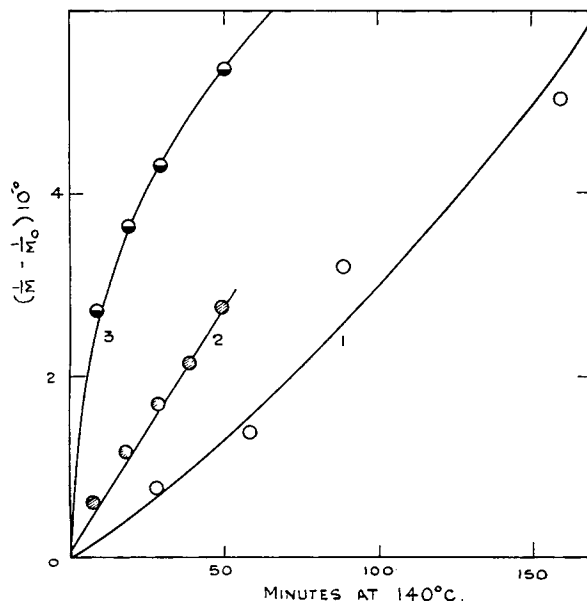


Fig. 3. Degradation of rubber (1) at 140°C. in films and on mastication at (2) 46 and (3) 105 rpm rotor speeds.

where the ordinate ( $1/M - 1/M_0$ ) expresses the moles of bonds cut per gram rubber,  $M_0$  and  $M$  being the molecular weights of the unmasticated and degraded rubbers, respectively.

Although its rate is influenced by applied shearing forces, hot mastication is still to be distinguished from cold mastication by being *primarily* dependent on the presence of oxygen. No degradation is detectable in the absence of oxygen with and without the presence of a radical acceptor. Results obtained with the greater control over mastication conditions with the laboratory masticator confirm the results previously obtained with the use of a Banbury mixer.<sup>1</sup> The physical measurements made provide, of course, no information on the chemistry of the hot-mastication reaction and an explanation of why it should be dependent on shear.

**Vulcanized Rubbers.** Consistent with the similarity of distribution of the masticated rubbers, the vulcanized rubbers processed by cold and hot mastication showed no differences in physical properties. Each series showed a dependence of  $C_1$  on initial molecular weight, in agreement with that previously observed for cold-masticated rubbers as revealed by the constancy of  $C_{1\infty}$  for each series. The values of  $\lambda^*$  and  $\nu_r$  were again similarly related to  $C_1$  for both series and confirmed relationships previously obtained for a wide range of vulcanized rubbers.<sup>13</sup>

The difference in Table IV between the degree of crosslinking of rubbers masticated at different temperatures and crosslinked by a common recipe were traced to variation occasioned by the separate compounding and vulcanizing of the different series. Molding small samples simultaneously greatly reduced the variation in degree of crosslinking observed.

In summary, cold and hot mastication to the same level of breakdown give masticated rubbers which are indistinguishable in properties influenced by chain-length distribution and yield vulcanizates of closely similar properties.

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### Synopsis

A comparison between the viscosity-molecular weight relationships for natural rubber degraded in thin films at 130 and 140°C. and on cold and hot mastication indicates a greater similarity of distribution on degradation by the mastication treatments. The hot mastication process is further differentiated from ordinary thermal reactions by the dependence of rate of degradation on the rate of shear. It does, however, differ from cold mastication in being primarily an oxidative-scission reaction. No differences were detected in the properties of networks prepared from rubbers masticated at high or low temperatures to the same level of degradation.

### Résumé

Si l'on compare les rapports existant entre la viscosité et le poids moléculaire dans le cas de caoutchouc naturel dégradé en minces films à 130 et 140°C et par malaxage à froid et à chaud, on constate une grande ressemblance de distribution après dégradation par les traitements de malaxage. Le processus de mastication à chaud se différencie en outre des réactions thermiques ordinaires par la dépendance de la vitesse de dégradation en fonction de la vitesse de malaxage. Il diffère néanmoins de la mastication à froid par le fait qu'il est en premier lieu une réaction de scission par oxydation. On n'a trouvé de différences dans les propriétés d'échantillons préparés à partir de caoutchoucs malaxés à hautes ou basses températures jusqu'au même degré de dégradation.

### Zusammenfassung

Ein Vergleich zwischen der Viskositäts-Molekulargewichtsbeziehung für Naturkautschuk, der in dünnen Filmen bei 130 und 140° abgebaut wurde, und der bei kalter und heisser Mastizierung vorhandenen, spricht für eine gross Ähnlichkeit der Verteilung beim Abbau durch die Mastizierungsmethoden. Der Prozess der heissen Mastizierung unterscheidet sich weiters von gewöhnlichen thermischen Reaktionen durch die Abhängigkeit der Abbaugeschwindigkeit von der Schubgeschwindigkeit. Von der kalten Mastizierung unterscheidet er sich jedoch dadurch, daß er primär ein oxydativer Spaltungsvorgang ist. Zwischen den Eigenschaften von Netzwerken, die aus Kautschuk durch Mastizierung bei hoher oder niedriger Temperatur zum gleichen Abbaugrad hergestellt wurden, konnte kein Unterschied festgestellt werden.

Received May 29, 1958