

Effect of Mastication on Molecular Weight and Molecular Weight Distribution of EPDM Polymer and SBR*

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Synopsis

EPDM and SBR were masticated on an open mill. The temperature range of mastication for EPDM was 68–480°F. SBR was milled at 170–200°F. The gel-permeation chromatography analyses were made on the masticated samples. For EPDM at 68°F, molecular weight decreases and molecular weight distribution narrows with mastication time; the degradation process is nonrandom. At constant mastication time between 182 and 315°F, there is little change in molecular weight. Mastication for 18 min at 480°F broadens the molecular weight distribution; the degradation is random. For SBR at 170–200°F, molecular weight decreases and molecular weight distribution narrows with mastication time; the degradation process is also nonrandom. Nonrandom degradation for both EPDM and SBR results in a narrowing of the molecular weight distribution, without build-up of low molecular weight molecules, and without a shift in the peak molecular weight. This is contrary to nonrandom degradation of natural rubber where a shift in the peak molecular weight occurs with mastication time.

INTRODUCTION

According to theoretical predictions^{1,2} the polymer molecular weight (MW) is reduced due to milling and attains a limiting value after a long milling time. It is also predicted² that a polymer with broad molecular weight distribution (MWD), when milled, will have a narrow MWD. A number of NRPR^{3,4} and other^{5,6} publications have provided the experimental evidence for the decrease of MW with mastication. At 125°F, for natural rubber, the MWD narrows with mastication time, and MW reduces to a limiting value after long milling time.

The present investigation is concerned with the changes in MW and MWD of an ethylene-propylene terpolymer and styrene-butadiene copolymer caused by the mastication.

EXPERIMENTAL

Ethylene-Propylene Terpolymer (EPDM)

EPDM (DuPont's Nordel 1070) was hot acetone-extracted for 32 hr and dried under vacuum at 50°C. No antioxidant was added to the

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extracted polymer. The dried polymer was stored in the dark in a nitrogen atmosphere until ready to masticate. The starting polymer was gel-free.

The mastication was done on an open mill. For room-temperature mastication, cold water was circulated through the rolls. For high-temperature mastication, hot oil was circulated through the rolls. The roll-surface temperature was taken as the mastication temperature.

The intrinsic viscosities and gel-content were determined as reported earlier.⁶ The gel-permeation chromatographic analyses were made on the masticated samples in 1,2,4-trichlorobenzene at 130°C. The samples were run through five columns packed with Styrogel. The columns had the following pore sizes: 60, 800, 10⁴, 10⁵, and 10⁶ Å. The rate of flow of the solution was 1 ml/min.

Styrene-Butadiene Rubber (SBR)

Two SBR rubbers of 1502 type were used for this study. The original Mooney viscosities ML-4 at 212°F of these rubbers were 155 and 56; both rubbers contained approximately 23% styrene. The mastication was done on an open mill. Mastication was started at room temperature and no attempt was made to control the roll-temperature. Both batches heated up very rapidly and equilibrated in the temperature range 170–200°F for most of the mastication period. Samples were removed after various milling times, immediately placed in sample bottles and flushed with nitrogen. These samples were dissolved in toluene containing Ionol (2,6-di-*tert*-butyl-*p*-cresol, Shell Chemical Co.), as a stabilizer within a few hours after sample removal. GPC analyses were run on toluene solutions at 85°C. The samples were run through four columns packed with Styrogel. The columns had the following pore sizes: 10³, 10⁴, 10⁵, and 10⁶ Å. The plate count on the columns was determined with a 1% solution of trichlorobenzene in toluene and found to be 1147 plates/ft.

RESULTS AND DISCUSSION

EPDM

Figure 1 shows the differential MWD curves for the samples masticated at 68°F for various times. Figure 2 shows the MWD curves for the samples milled for 30 min at different temperatures. Table I lists the GPC molecular weights, intrinsic viscosities, and the gel content of the samples. The GPC molecular weights should not be taken as absolute MW of the samples.

The data show that at 68°F, the molecular weight decreases and the MWD narrows down with the mastication time. After 60 min of mastication (Curve *D* in Fig. 1), the maximum MW is reduced from 20.15×10^5 to 8.52×10^5 . However, as expected, the low ends are practically unaffected at this temperature. This means that at low temperature the

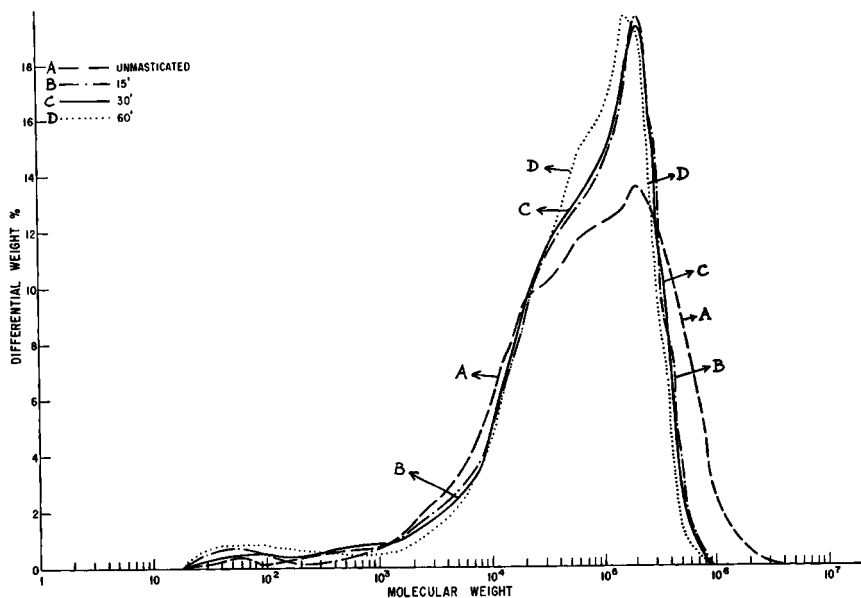


Fig. 1. GPC differential MWD of EPDM polymers masticated at 68°F: (A) unmodified; (B) masticated 15 min; (C) 30 min; (D) 60 min.

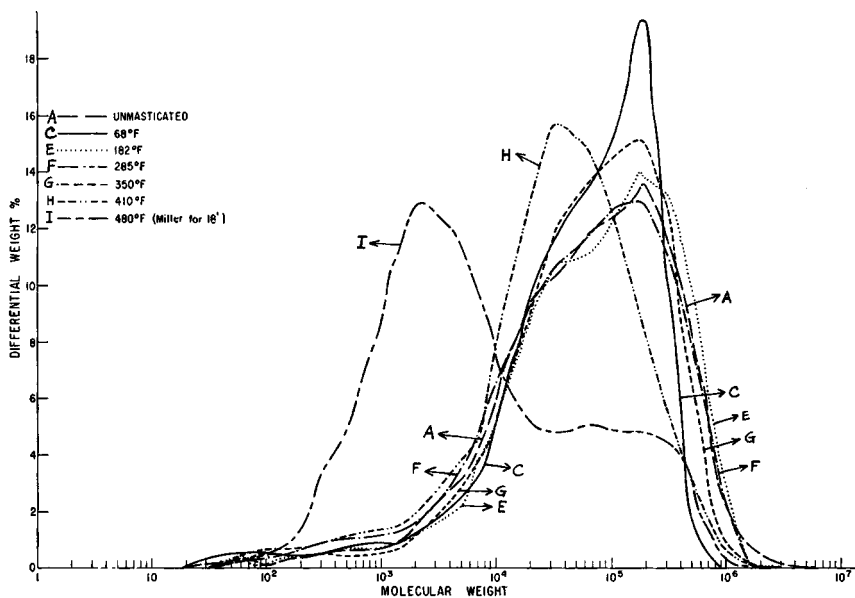


Fig. 2. GPC differential MWD of EPDM polymers masticated at different temperatures for 30 min: (A) unmodified; (C) 68°F; (E) 182°F; (F) 285°F; (G) 350°F; (H) 410°F; (I) 480°F (milled for 18 min).

TABLE I
 GPC Molecular Weights of EPDM Masticated Samples

Sample	Time of milling, min	Milling temp, °F	GPC molecular weights					Gel, %	
			$\bar{M}_w \times 10^{-4}$	\bar{M}_n	Max. $\times 10^{-6}$	Min.	Peak $\times 10^{-4}$		$[\eta]$
A (control)	0	—	15.68	3862	20.15	20	16.9	3.55	0
B	15	68	11.28	2464	9.23	22.1	15.6	2.27	4.1
C	30	68	10.64	3027	8.58	24	15.0	2.17	3.8
D	60	68	9.93	1669	8.52	22.1	13.4	1.95	3.4
E	30	182	16.82	2869	16.25	29	20.4	3.32	1.0
F	30	285	14.41	2838	16.25	17	15.3	3.40	0.7
G	30	350	13.1	4562	14.3	31	16.3	2.20	0.7
H	30	410	8.365	2923	14.3	26	3.8	1.50	0.4
I	18	480	4.73	1411	10.01	30	2.6	0.50	0

larger molecules are broken down preferentially and the polymer degradation is a nonrandom process.

It is interesting to note that even though the change in the maximum MW with mastication is considerable, the peak MW changes very little.

Let us now compare the MWD curves in Figure 2. The sample C, milled at 68°F for 30 min, has the narrowest MWD. Up to 350°F, there is not much change in peak MW except for sample E in which case probably more recombination takes place. Above 350°F, the peak MW decreases considerably and the MWD is very broad, especially at 480°F. It should be pointed out that even at 480°F, some of the larger molecules are not broken down. However, the low MW species increase in number. These observations indicate that at 480°F, the degradation process, which is thermo-oxidative,⁶ is a random one. This verifies Bueche's prediction that at very high temperature, the degradation process is random.

A considerable difference exists in the GPC molecular weights of samples C and E. The MW and $[\eta]$ values of sample C are lower than for sample E. The reason for this difference is simple. At 68°F (sample C), due to the higher shearing force, the sample is more degraded than at 182°F.

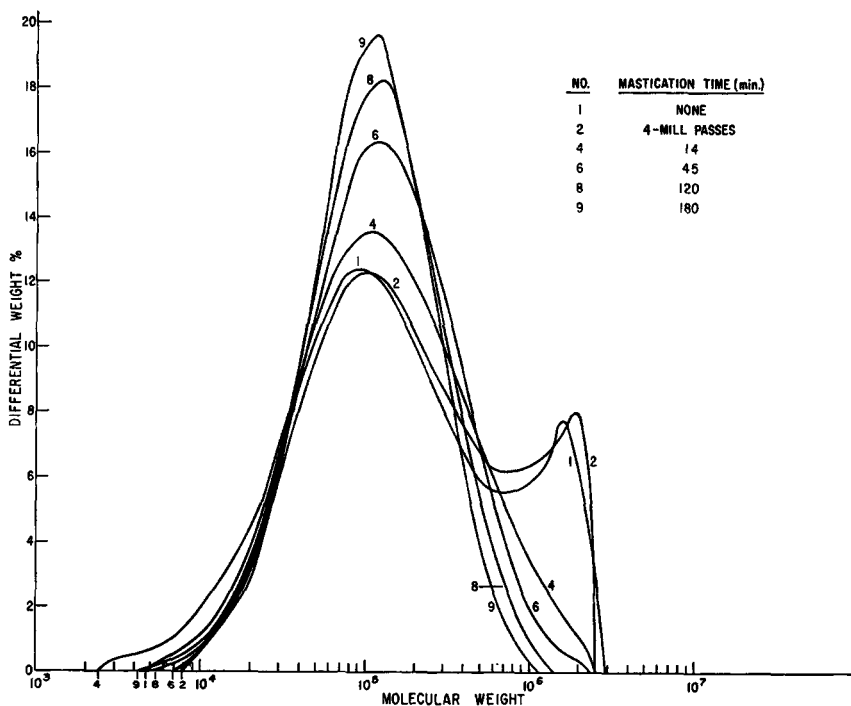


Fig. 3. GPC differential MWD of high molecular weight SBR masticated at 170-200°F for various times: (1) unmasticated; (2) 4 mill passes; (4) 14 min; (6) 45 min; (8) 120 min; (9) 180 min.

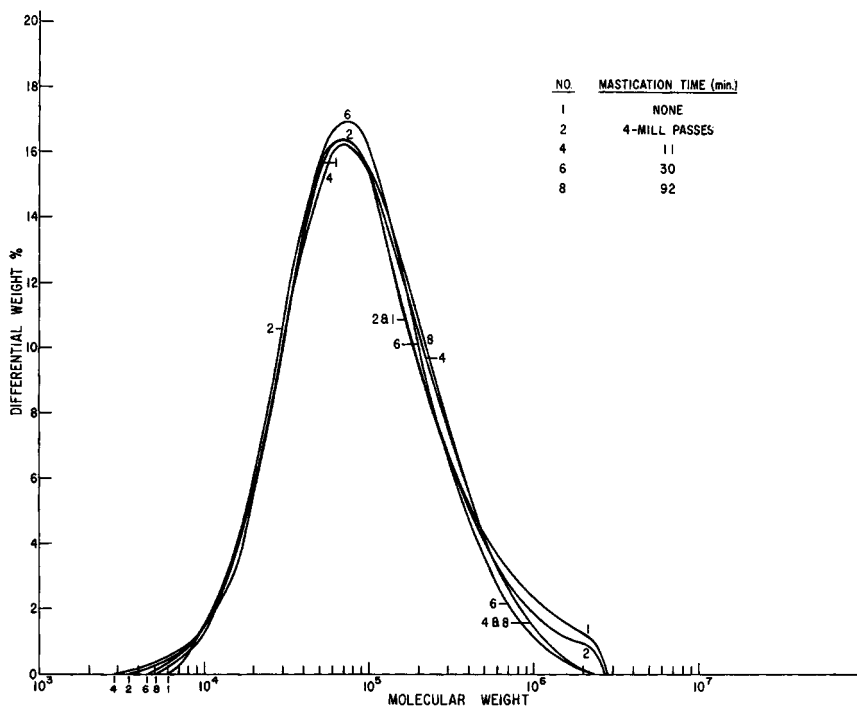


Fig. 4. GPC differential MWD of low molecular weight SBR masticated at 170–200°F for various times: (1) unmasticated; (2) 4 mill passes; (4) 11 min; (6) 30 min; (8) 92 min.

SBR

MWD obtained from GPC have been plotted in Figures 3 and 4. The actual values are given in Table II. It can be seen that the two SBR materials used in our study differed both in MW and MWD. Note that all of the data collected have not been plotted to prevent cluttered graphs.

The data show that mill-mastication of SBR, at 170–200°F, causes a narrowing of the distribution primarily through the breaking down of high MW molecules. However, contrary to the case with natural rubber,⁵ the primary peak of the distribution curve does not shift significantly. For example, the peak MW of high molecular weight SBR hovers around 10.0×10^4 while the lower molecular weight SBR hovers around 7.0×10^4 . In this respect, EPDM and SBR behave very much alike. It should be understood that these molecular weights are not absolute values. This fact, however, does not detract from the conclusions drawn.

Like the peak MW, the \bar{M}_n shows no regular reduction, instead it shows a rather erratic change about an average value. Regular changes in the high MW SBR can be seen by a progressive lowering of \bar{M}_w and \bar{M}_w/\bar{M}_n ratio. The low molecular weight SBR shows an irregular decline in these values with a leveling out at 20–30 min milling.

The MWD curves clearly show that high MW tails are broken down. The wavering, back and forth, of the low MW portion of the distribution curves as well as the wavering of the peak and \bar{M}_n values are considered as indirect evidence that recombination of broken polymer molecules occurs to a significant degree during SBR milling.

The per cent solids was determined on the GPC samples before and after the normal sample filtration procedure. The per cent polymer filtered out is given in Table II. The fact that this tends to be so variable

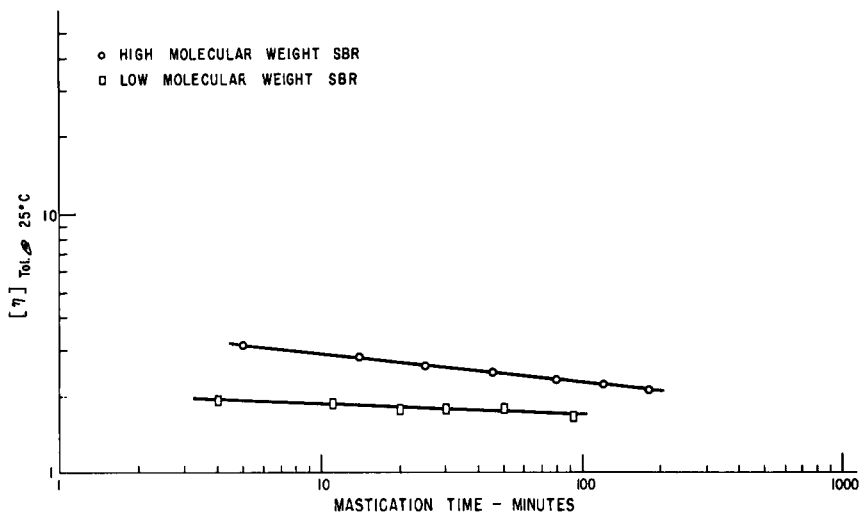


Fig. 5. Intrinsic viscosity vs. mastication time for SBR: (O) high molecular weight SBR; (□) low molecular weight SBR.

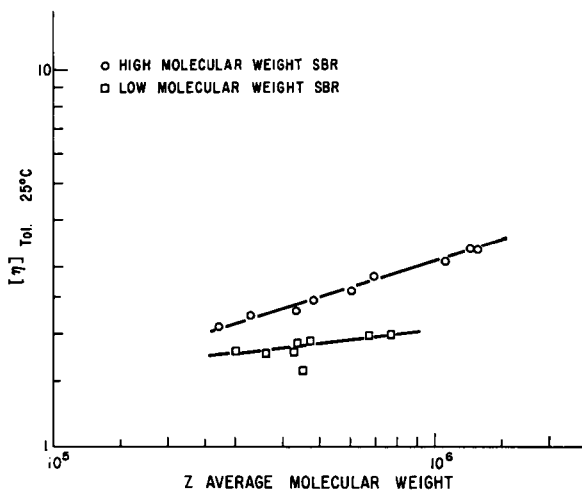


Fig. 6. Intrinsic viscosity vs. Z-average molecular weight: (O) high molecular weight SBR; (□) low molecular weight SBR.

TABLE II
Masticated SBR Molecular Weight from Gel-Permeation Chromatograph

Sample	Mastication time, min	GPC molecular weights						Gel, % ^b	
		$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-4}$	Peak $\times 10^{-4}$	\bar{M}_w/\bar{M}_n	Max. $\times 10^{-6}$	Min. $\times 10^{-3}$		$[\eta]^a$
High molecular weight SBR									
1	None crumb	4.12	7.26	9.30	5.68	2.87	4.6	3.38	9.0
2	4 mill passes	4.58	8.83	9.70	5.18	2.49	7.6	3.35	25.0
3	5	3.57	8.07	8.70	4.42	2.91	5.7	3.11	6.5
4	14	2.35	5.29	10.44	4.45	2.50	2.4	2.84	7.2
5	25	2.26	7.01	11.50	3.22	2.53	4.0	2.60	8.2
6	45	2.04	7.79	11.50	2.62	2.35	6.8	2.45	9.7
7 ^c	80	1.88	5.51	11.60	3.42	2.23	1.8	2.30	9.6
8	120	1.67	7.26	10.80	2.30	1.40	5.0	2.23	5.6
9	180	1.48	6.81	9.60	2.16	1.17	4.2	2.10	7.3
Low molecular weight SBR									
1	None-crumb	1.98	5.74	6.80	3.44	2.79	5.7	1.99	2.6
2	4 mill passes	1.74	5.22	6.80	3.34	2.72	3.4	1.98	3.4
3	4	1.62	4.93	7.10	3.27	2.43	2.6	1.91	0.7
4	11	1.54	5.22	7.40	2.95	2.41	2.8	1.88	25.4
5	20	1.38	4.73	6.80	2.92	1.59	2.3	1.77	6.5
6	30	1.43	5.26	7.30	2.72	2.28	4.5	1.79	10.1
7	50	1.37	5.45	7.70	2.52	1.26	3.6	1.80	6.0
8	92	1.55	5.51	7.40	2.80	2.35	5.1	1.60	6.0

^a In toluene, 25°C.

^b Per cent filtered out in GPC before MW and MWD determination.

^c Long flow tailout which made cut-off difficult to locate. \bar{M}_n value is probably much too low.

and relatively large is additional evidence that recombination is a significant phenomenon in SBR mastication. The nature of this gel is unknown, i.e., whether it is due to highly branched crosslinked molecules or extremely large linear crosslinked molecules. Because of the amount filtered out of the GPC samples, the distribution curves pertain to only sol portion of the polymers. It should also be noted that the distribution curves of the original and slightly milled samples do not resolve the high MW molecules very well.

In Figure 5 a log-log plot of intrinsic viscosity versus mastication time can be found. This graph shows that the breakdown rate of the high molecular weight SBR is greater than that of the low molecular weight SBR. This is to be expected if one accepts the mechanical degradation theory of Bueche,² which indicates that the rate of degradation is directly dependent upon the molecular weight. Figure 6, a log-log plot of intrinsic viscosity versus *Z*-average molecular weight, emphasizes the large differences between the high molecular weight portions of these two SBR rubbers throughout their entire mastication periods.

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