

## Degradation of Natural Rubber during Mill Mastication

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### Synopsis

Changes in the molecular weight distribution of natural rubber, after mill mastication, have been studied by using a Water's gel permeation chromatograph. This study indicates that as the polymer is milled the distribution is narrowed primarily through the breaking down of large molecular weight molecules. The peak of the distribution curve shifts to lower and lower molecular weight with increased milling time but it appears to be approaching a limiting molecular weight after 76 min. of milling time. One unexpected result is the development of a secondary hump in the distribution curve at the high molecular weight end. This hump gets larger and moves to lower molecular weight with increasing milling time until 76 min. of milling, at which time it disappears entirely.

### INTRODUCTION

Mastication of natural rubber has been studied by numerous investigators. Busse<sup>1</sup> and Busse and Cunningham<sup>2</sup> studied the breakdown of natural rubber during milling as early as 1932. They concluded that the more rapid breakdown at temperatures  $>240^{\circ}\text{F}$ . was principally due to rapid oxidation while at temperatures  $<240^{\circ}\text{F}$ . the breakdown rate probably involved "mechanical activation."

Various members of the NRPRRA have studied numerous aspects of the mastication of natural rubber over a number of years. Pike and Watson<sup>3</sup> cold-masticated natural rubber and concluded that degradation is caused by mechanical rupture of primary carbon-carbon bonds to give polymer radicals which are stabilized by oxygen giving degraded polymer molecules. Subsequent studies by Ayrey et al.<sup>4</sup> verified that polymer radicals are stabilized by interaction with radical acceptor molecules, such as 1,1-diphenyl-2-picryl hydrazyl, giving degraded polymer.

Angier et al.<sup>5</sup> cold-masticated natural rubber, determined viscosity-molecular weight relationships, and proposed a mechanism of rupture during mastication. It was concluded that monomeric units in long chains have a greater probability of rupture than those in short chains. This conclusion was supported by reference to a mechanism proposed by Frenkel.<sup>6</sup> Frenkel stated that a polymer molecule of chain length greater than a critical value,  $X_0$ , becomes extended when sheared and eventually ruptures at a bond near the center section between terminal segments of length

$X_0/2$ . Molecules less than  $X_0$  in length are not considered to be ruptured under fixed shear conditions.

Bueche<sup>7</sup> has proposed a molecular theory for the mechanical degradation of high polymers. The validity of this theory depends upon the presence of molecular entanglements. It is stated that these entanglements give rise to very large tensions near the central portions of the molecules. The theory indicates that, for a given chain molecular weight, approximately 10 chains will break at the center for each chain which breaks  $1/3$  of the way out from the center. This theory predicts that if a polymer has a molecular weight distribution which is broad, it will be narrowed by mastication and under fixed shear conditions will approach a limiting molecular weight. It is also predicted that the breakdown rate is a rapidly varying function of molecular weight, being very rapid for high molecular weight and greatly reduced for lower molecular weight.

With the advent of the Water's gel permeation chromatograph it is now possible to obtain molecular weight distribution curves with much less expenditure of time and effort. Changes in the molecular weight distribution of natural rubber, after mill mastication, have been studied by using this instrument.

### Experimental

A 2000-g. sample of natural rubber (No. 1 RSS), was masticated on a 10-in. laboratory mill. Frictional heat caused the batch to attain a temperature of approximately 125°F. The roll setting was such that after a smooth sheet had formed its thickness was approximately 0.120 in. This sample was continuously masticated for a total time of 76 min. Samples were removed after various milling times, immediately placed in sample bottles, and flushed with  $N_2$  for 1 min. These samples were dissolved in trichlorobenzene containing Ionol (2,6-di-*tert*-butyl-*p*-cresol, Shell Chemical Co.) as a stabilizer within a few hours after sample removal. These samples were run in the Water's gel permeation unit at 130°C.

### Discussion

The molecular weight distributions obtained from the gel permeation analysis have been plotted in Figure 1 as a function of the height readings taken from the original recorder plot.

By examining the shape of the distribution curves the following conclusions can be drawn. As the polymer is milled, the distribution is narrowed primarily through the breaking down of large molecular weight molecules. The peak of the distribution curve shifts to lower and lower molecular weight with increased milling time. One unexpected result is the development of the hump at the high end of the curve. This hump becomes larger and moves to lower molecular weight with increasing milling time until 76 min. of milling, at which time it disappears entirely. One possible explanation for the appearance of this hump is that as the large molecules are broken by the shearing action of the mill, some of them recombine to form

TABLE I

Sam- ple	Milling time, min.	Molecular weight					$\bar{M}_w/\bar{M}_n$
		$\bar{M}_w$ $\times 10^{-3}$	$\bar{M}_n$ $\times 10^{-3}$	Peak $\times 10^{-3}$	Max. $\times 10^{-6}$	Min. $\times 10^{-3}$	
A	8	602.4	75.5	288.6	13.9	1.7	7.89
B	21	573.8	47.7	150.0	19.5	1.1	12.10
C	38	360.2	39.5	87.0	19.5	1.7	9.10
D	43	340.9	48.1	80.0	11.8	1.7	7.08
E	56	514.3	43.1	73.0	12.9	1.6	12.00
F	76	98.1	34.7	60.0	1.3	1.5	3.11

a few molecules of even larger molecular weight than was present in the sample which had been milled for 8 min. There was a small amount of gel in the 8 min. sample which was removed by our filtration process. As the process of shearing, breakdown, and recombination continues, we have essentially the formation of a bimodal distribution.

The values of various weights calculated from the GPC graphs are given in Table I.

The discontinuity caused by sample E can be explained by the rapid increase in the size of the small peak at the high end. Since in the calculation of  $\bar{M}_w$  the larger molecules are weighted so much more than the small,  $\bar{M}_w$  for this sample becomes quite large and  $\bar{M}_w/\bar{M}_n$  likewise becomes large. If one were to ignore the peak which develops at the high end, one would

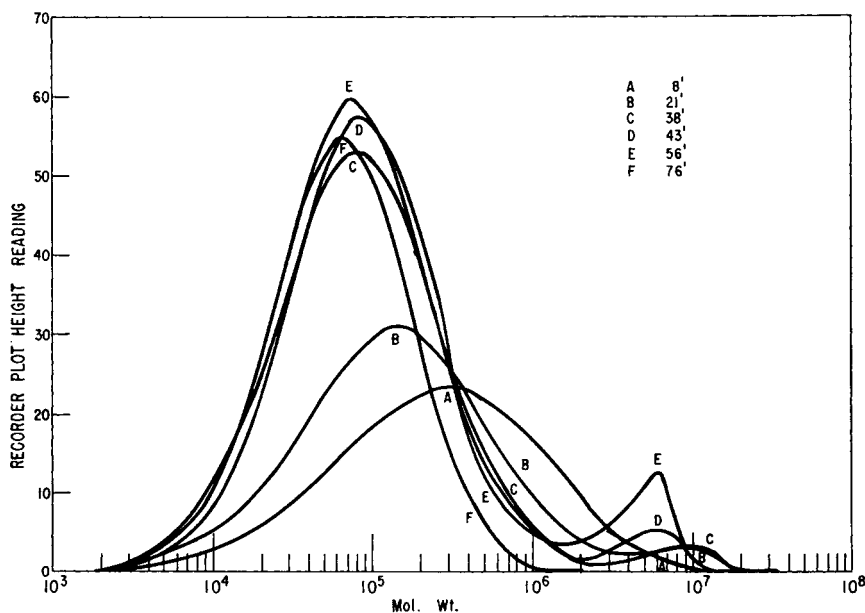


Fig. 1. Water's gel permeation analysis of natural rubber mastication.

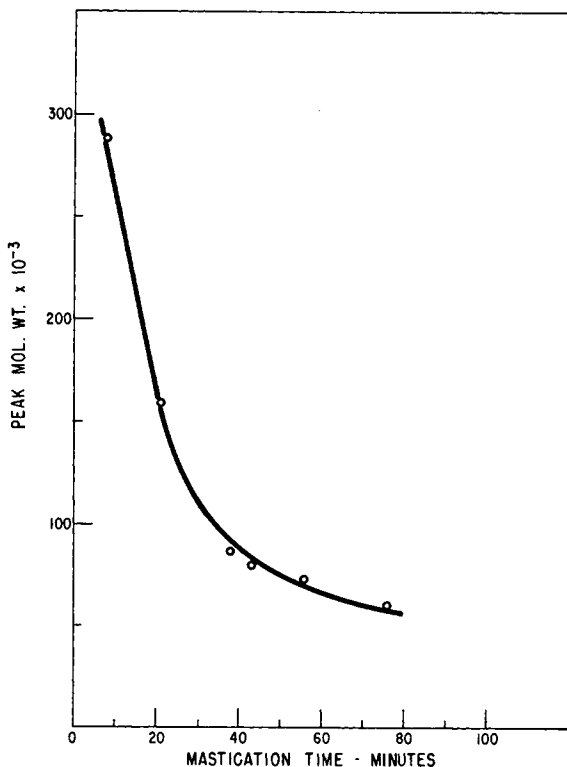


Fig. 2. Variation of peak molecular weight with mastication time.

see a steady decrease in  $\bar{M}_w$  (peak) and  $M_w/M_n$  with almost no change in  $\bar{M}_n$ .

Sample A may very possibly also have been a bimodal distribution, since a small amount of gel ( $\approx 1-2\%$ ) was filtered out of this sample. Also, it is not consistent that the maximum molecular weight of sample A ( $13.9 \times 10^6$ ), should be lower than for sample B ( $19.5 \times 10^6$ ). In fact, it is also possible that a small amount of material, not easily observed, was filtered out of sample B, since its maximum molecular weight should be somewhat higher than that of sample C and not equal to it.

The molecular weight data from the Water's instrument may not necessarily compare exactly with the more absolute methods of molecular weight determination; however, they are all relative and the right order of magnitude. The data plotted in Figure 1 indicate an approach to a limiting peak molecular weight. In addition, there is essentially no change in the minimum molecular weight of all samples examined, even though the permeation instrument can readily detect lower weights. A further point to note is the similarity in shape and near coincidence of the low molecular weight half of the distribution curves for samples C, D, E, and F. It is also interesting to note that the peak height change from sample A to sample B represents a decrease by approximately a factor of 2, while from

sample B to sample C the decrease is again approximately a factor of 2. This represents an average of one chain scission, in the bulk of the molecules, in each successive step from sample A to sample B to sample C.

The peak molecular weight of the major peak has been plotted as a function of the mastication time in Figure 2. It is apparent that breakdown is very rapid for approximately 20 min., followed by a rapidly decreasing rate which has become almost zero after 76 min. of mastication.

The results of this study support the original proposal of Frenkel and the molecular theory proposed by Bueche. Quantitative verification of Bueche's theory will be the subject of more precisely controlled future experiments.

### References

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### Résumé

Des variations de distribution de poids moléculaire de caoutchoucs naturels, après mastication, ont été étudiées en utilisant le chromatographe à perméation au gel de Water. Cette étude indique que si le polymère est broyé, la distribution est rendue plus étroite au début par suite de la rupture des molécules de poids moléculaire élevé. Le pic de la courbe de distribution glisse vers des poids moléculaires de plus en plus faibles avec une durée de broyage prolongée mais s'approche d'un poids moléculaire limite après un temps de broyage d'environ 76 minutes. Un résultat inattendu est le développement d'un second maximum dans la courbe de distribution du côté des poids moléculaires élevés. Ce maximum devient plus large et se déplace vers des poids moléculaires plus bas avec des temps de broyage croissant jusque 76 minutes, temps à partir duquel ce second maximum disparaît complètement.

### Zusammenfassung

Die Änderung der Molekulargewichtsverteilung von Naturkautschuk bei der Mastizierung auf der Walze wurde mit einem Waters-Gelpermeationschromatographen untersucht. Die Untersuchung zeigt, dass die Verteilung beim Walzen des Polymeren primär durch die Spaltung der hochmolekularen Moleküle verengt wird. Das Maximum der Verteilungskurve verschiebt sich mit steigender Walzdauer zu einem niedrigeren Molekulargewicht, scheint sich aber nach 76 min Walzdauer einem Grenzmolekulargewicht zu nähern. Ein unerwartetes Ergebnis ist die Engwicklung eines sekundären Höckers in der Verteilungskurve am hochmolekularen Ende. Dieser Höcker wird mit zunehmender Walzdauer grösser und bewegt sich zu niedrigerem Molekulargewicht bis zu einer Walzdauer von 76 min; bei dieser verschwindet er völlig.

Received October 5, 1965

Prod. No. 1300