

Stress–Strain Effects of Mechanically Degraded Natural Rubber Latex

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SYNOPSIS

A well-characterized fresh natural rubber latex with total solids content of 42.1% was subjected to high-speed mechanical stirring for over 6 h. Mechanical and solution studies on samples withdrawn at intervals showed clearly that rubber degradation occurred within 4–5 h of continuous stirring. Such degradation in the liquid phase is considered to be of industrial importance in the rubber industry. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The process of mechanical degradation of natural rubber takes place in a number of ways, e.g., cold mastication, milling, extrusion, blending, vibromilling, as well as high-speed stirring, shaking, and shearing of rubber solutions.¹ The viscosity of natural rubber is too high for processing; it is therefore lowered by the process of mastication discovered by Hancock² in which the molecules are broken down from molecular weight of about 10^7 to values of 20,000–30,000. The chemical nature of mechanical degradation was elucidated by Pike and Watson,³ Ceresa and Watson,⁴ and Besse and Cunningham.⁵ Pike and Watson showed that there is an increase in the number of molecules during the mastication of solid natural rubber. Ceresa and Watson in their work found that macro-radicals produced by mechanical scission of the polymer molecule were effective initiators for radical polymerization in the absence of oxygen. During mastication, Busse and Cunningham found three effects on natural rubber. They are:

1. At 100°C mechano-degradation of solid natural rubber is minimal.
2. Below this temperature, the dominant pro-

cess is mechanical shear, which increases with increasing polymer viscosity.

3. Above 100°C, the process of radical initiated oxidation becomes more important.

However, the mastication of solid natural rubber in nitrogen produced no changes in the system.^{2,6} This was interpreted as scission that occurred between isoprene units in which the radicals formed were stabilized by resonance and finally recombined.

Solid natural rubber when mechanically degraded provides molecules of different sizes which could be adapted for various uses as a polymeric chemical intermediary, such as in block and graft copolymerization reactions¹ and in the incorporation of antioxidant and antifatigue agents.⁷

The mechanical degradative processes on natural rubber are either on the solid coagulum or its solution. No work has been reported on the mechanical degradation of the raw natural rubber latex. Most polymers, whether synthetic or natural, are derived from the latex. The polymer molecules in the latex and the coagulated materials are the same; thus as further processing of the coagulum leads to molecular fracture, so also it is hoped that mechanical work when imposed on the latex would also result in substantial changes in the molecular arrangement and dimensions. Differences can only be attributed to the aqueous phase in which the rubber molecules are dispersed in the latex. The work on the mechanical degradation of the fresh natural rubber latex through high-speed stirring is presented here.

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EXPERIMENTAL

Materials and Equipment

The following materials and equipment were used: Fresh field natural rubber latex obtained from the Imo Rubber Estates, Ltd., Obitti, Ohaji, Nigeria; concentrated ammonia solution (BDH); toluene (BDH); methanol (BDH); isooctylphenoxyethoxyethanol (Triton X-100), a nonionic surfactant (BDH); Brookfield viscometer; Ubbelohde viscometer; Instron Universal Testing Machine Model 1122; and a mechanical stirrer.

Method

All chemicals used were analytical grades and used as such. The fresh latex was collected in a stoppered bottle and stabilized by adding 25 cm³ concentrated ammonia solution to 2.5 L of the latex (1.0% v/v). The latex characteristics are as determined⁸ and shown in Table I.

Degradation

The method of degradation involved the following steps:

Construction of the Mechanical Stirrer

A shaft 45 cm long and 2.5 cm in diameter carrying three baffles (3.0 × 6.0 cm each) was welded to the shaft of an electric motor (50 Hz; 4.0 kW; 380 V; 8.9 A) having a constant speed of 1440 rpm. A hole was created through the lid of a stainless bucket (which served as a reactor) through which the stirrer shaft was passed. The stirrer was mounted on a tripod.

Preparation of the Latex

Fresh natural rubber latex was diluted to approximately 15.0% by adding 3.5 L of distilled water to 2.0 kg of the latex. Then 60.0 g Triton X-100 surfactant (3.0% w/w on the latex) was added, and the mixture was gently stirred for 1 h to attain maximum stabilization before the degradation stage.

Mechanical Degradation

The prepared latex was stirred with the mechanical stirrer. Samples were collected at intervals and filtered under pressure to exclude gelled lumps of rubber. The viscosity of the filtrate was measured with a Brookfield viscometer. The latex was later coagulated with methanol. The coagulum was rolled into

sheets of about 3.0 mm, washed extensively in running water, and dried in an oven at 50°C for 48 h to a constant weight.

Measurement of Mechanical Properties

The dried degraded coagula were cast into thin sheets of approximately 1.0 mm thickness by evaporating 100 cm³ of 2.0% rubber solution in toluene at room temperature for 72 h and drying to a constant weight in an oven at 50°C for 24 h. The casts were cut into strips of 1.0 × 6.0 cm each for tensile strength measurements.

The tensile strength of the degraded rubber samples were measured with an Instron Universal Testing Machine Model 1122 with the following constants:

$$\begin{aligned} \text{Full-scale load} &= 1.0 \text{ kg} \\ \text{Crosshead speed} &= 50 \text{ mm/min} \\ \text{Chart speed} &= 100 \text{ mm/min} \\ \text{Gauge length} &= 30 \text{ mm} \end{aligned}$$

Stress-strain plots were determined from which the moduli, elongation at break, and tensile strengths of the degraded samples were derived.

Molecular Weight Determinations

Viscosity-average molecular weights (\bar{M}_v) were determined through viscometry in a Ubbelohde viscometer maintained at 25 ± 0.1°C in a water bath. Viscosity-average molecular weights were calculated using the Mark-Houwink equation^{9,10}:

$$[\eta] = K\bar{M}_v^a$$

where k and a are constants dependent on the solute, solvent, and temperature; k and a values of 5.02×10^{-4} and 0.662, respectively, in toluene at 25°C for natural rubber were taken from *Polymer Handbook*.¹¹

Table I Characteristics of the Natural Rubber Latex

Viscosity-average molecular weight (\bar{M}_v)	= 1.31 × 10 ⁶
Dry rubber content (DRC) (%)	= 41.30
Ash content (%)	= 0.21
Nitrogen content (%)	= 0.60
Volatile matter (%)	= 0.62
Dirt content (%)	= 0.02
Plasticity retention index (PRI) (%)	= 56.82

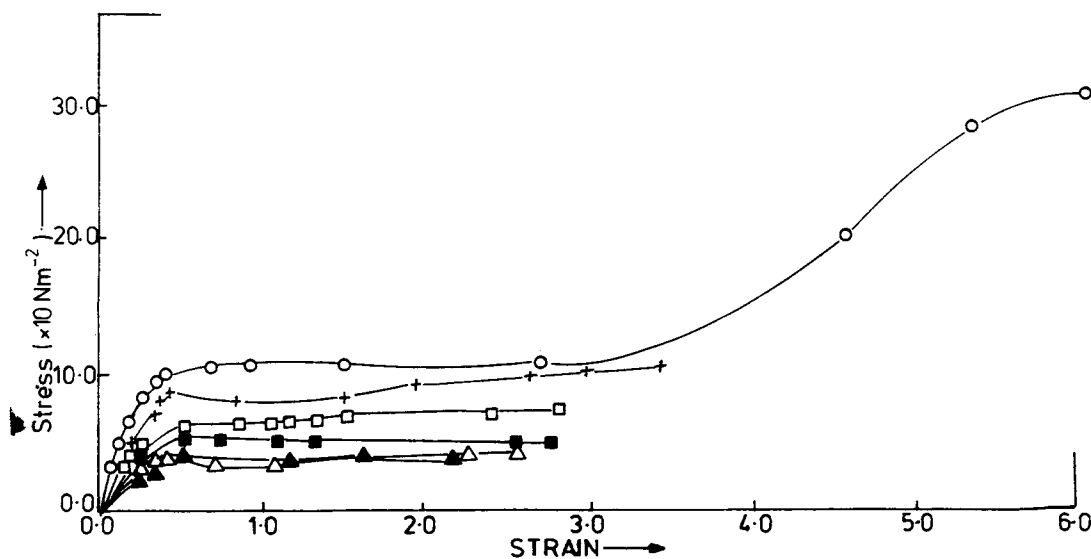


Figure 1 Stress-strain curve for the degraded natural rubber latex. (○—○) Undegraded (0.0 h) rubber, (+—+) 0.5 h degraded rubber, (□—□) 1.0 h degraded rubber, (■—■) 2.0 h degraded rubber, (△—△) 3.0 h degraded rubber, and (▲—▲) 4.0 h degraded rubber.

RESULTS AND DISCUSSION

The characteristics of the field latex as determined are shown in Table I.

Mechanical Properties

Figure 1 shows the stress-strain plots of the degraded natural rubber samples. Separation of the

individual curves is obvious, which indicates that degradation occurred during the shearing process. This is further supported by the other parameters derived from the stress-strain curves, namely modulus and elongation at break, as shown in Table II.

Modulus

Modulus, or stiffness, is a measure of the compactness and molecular weight of polymer molecules. Polymers of high molecular weights show high modulus. The modulus of the degraded rubber samples decreased from $5.217 \times 10^4 \text{ N m}^{-2}$ to $1.176 \times 10^4 \text{ N m}^{-2}$ in 5 h as shown in Figure 2. The decrease shows that mechanical degradation occurred during the shearing process, which led to the formation of shorter chains.

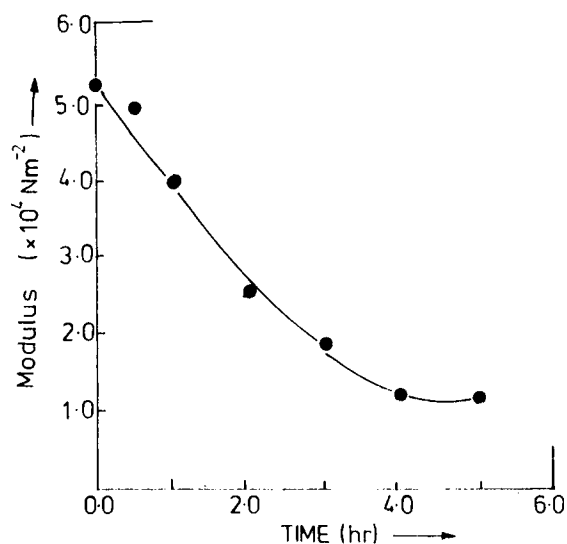


Figure 2 Graph showing variation of modulus of the degraded samples with time of degradation.

Table II Changes in Modulus and Elongation at Break with Time of Degradation

Time (h)	Modulus ($\times 10^4 \text{ N m}^{-2}$)	Elongation at Break (%)
0.0	5.217	1310.000
0.5	5.014	786.000
1.0	4.000	650.833
2.0	2.909	649.000
3.0	1.882	602.333
4.0	1.176	534.133
5.0	1.176	483.333

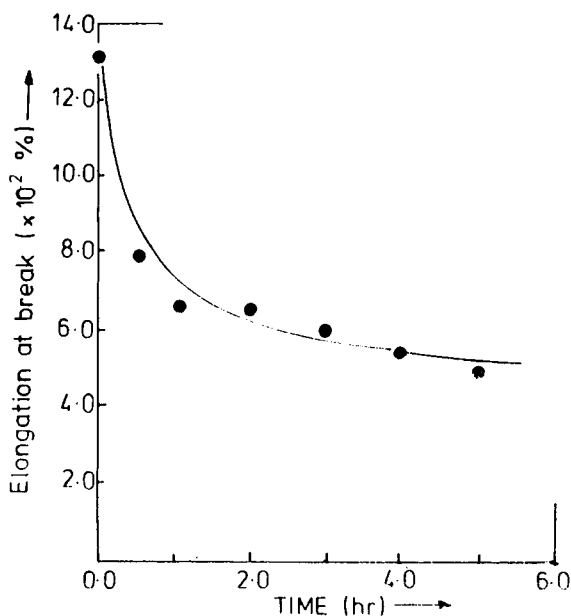


Figure 3 Variation of elongation of degraded samples with time.

Elongation at Break

It was observed that the undegraded natural rubber showed a very high elongation at break (1310.00%). After 30 min of degradation the elongation was reduced to about half (786.00%). During this period maximum breakdown of the rubber molecules took place. This is so because the elongation of the others were not too far from each other as shown in Table II. Elongation is the effect brought about by uncoiling the randomly entangled chains through axial stretching. Breakage occurs when the chains have exceeded the maximum stretched length. The results of elongation therefore suggested that the rubber chains were broken somewhere midway along the chains during the first 30 min of stirring (1310–786%). Alternatively, it could mean that during the initial stage of stirring, the nonrubber contents in the latex, such as the natural stabilizers, suffered the greatest breakdown, which subsequently exposed the higher molecular weight and lengthy chains of the rubber particles to the shearing force which broke them up. Thereafter the resulting surrounding medium offered little or no resistance to the shearing forces and so permitted direct transfer of force to rubber molecules.

Figure 3 shows decrease in elongation and indicates extent of degradation; the maximum degradation is reflected by the corresponding minimum value of elongation, since strain or elongation is proportional to chain length. The almost constant

value beyond 4 h of degradation indicates that the chain lengths have been reduced to a constant value which can no longer be affected by the shearing forces applied.

Brookfield Viscosity

Figure 4 shows the variation of Brookfield viscosity with time of stirring. There was rapid degradation of the rubber molecules in the first 30 min as shown by the drastic change in viscosity. Most of the breakdown occurred within 1 h. A gradual decrease in viscosity resulted after 1 h up to the fourth hour; thereafter the degradation process was virtually complete as indicated by the near horizontal nature of the curve in this period. This confirms the results from stress-strain measurements. The constant viscosity shows that the average molecular weight has assumed a constant value, and there is no further reduction in the chain lengths or molecular size with further application of the given shearing stress.

Viscosity-Average Molecular Weight (\bar{M}_v)

Figure 5 shows viscosity-average molecular weight versus time of degradation. The molecular weight decreased from 1.313×10^6 to 0.212×10^6 in 5 h of mechanical action. The high reduction (about 84%) in molecular weight shows that stirring of the natural rubber latex is an effective method of achieving mechanical degradation.

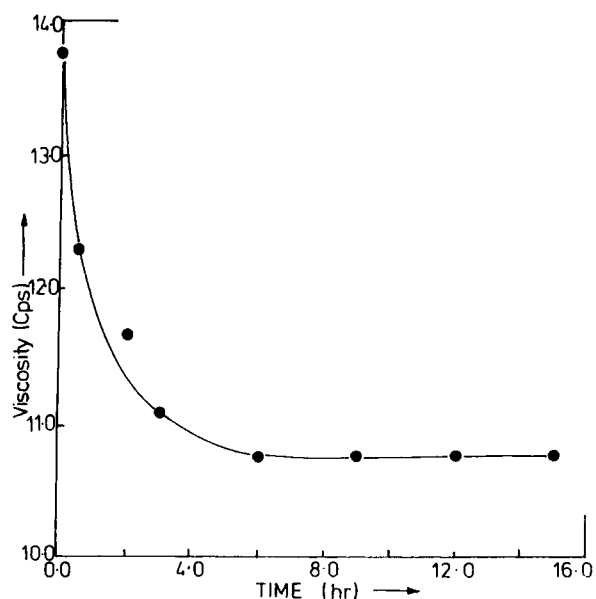


Figure 4 Brookfield viscosity measurement during latex degradation.

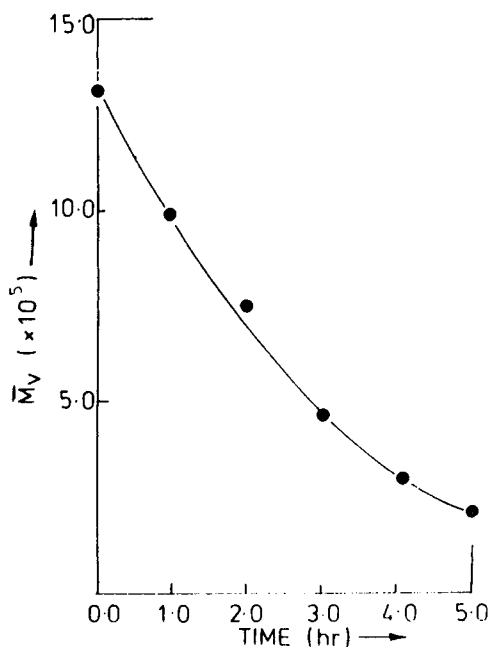


Figure 5 Variation of viscosity-average molecular weight (\bar{M}_v) with time of degradation.

CONCLUSION

Results obtained from this work indicate that rubber hydrocarbon molecules are easily broken down by high-speed stirring of the fresh latex. Before now all mechanical degradations of natural rubber were based on the mastication of the solid rubber either in an internal mixer or in a two-roll milling machine.

Mechanical degradation of solid dry rubber re-

quires the use of expensive machinery, as is in vogue in industries. It is hoped that by adopting the process of latex degradation, a much cheaper and easier approach is achieved.

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