

Storage Hardening and "Abnormal" Groups in Guayule Rubber*

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Synopsis

The hardening process of natural (*Hevea brasiliensis*) rubber, that takes place when this rubber is stored in dry conditions over long periods of time, has been correlated with the presence of reactive "abnormal" groups directly grafted on the polymeric chain and in the serum of the latex. In the present work, natural Hevea (HR) and Guayule (*Parthenium argentatum*) rubber (GR) were stored under accelerated conditions and the changes in Mooney viscosity and molecular weight measured. The results showed that while HR undergoes hardening, GR keeps its Mooney viscosity constant, as does a constant viscosity (CV) Hevea rubber. These results are explained by the absence of functional "abnormal" groups that sustain the hardening reactions.

INTRODUCTION

The chain of natural HR is not pure *cis* 1,4 polyisoprene but has certain "abnormal" groups^{1,2} that can undergo condensation³ and addition⁴ reactions; these reactions are responsible for the hardening of the rubber that occurs when it is stored over long periods of time,⁵ especially under dry conditions.

The functional groups have been identified as aldehydes⁶ and epoxides⁷ grafted onto the polymeric chain and amino groups,^{2,3} mainly present in the proteins of the serum phase of latex. The presence of carbonyl groups is not due to oxidation of the rubber chain during or after the extraction from the tree, because groups are present even in samples extracted⁸ in the absence of oxygen. However, the rubber from Guayule (*Parthenium argentatum*, Gray) is a *cis* 1,4 polyisoprene⁹ with a molecular weight similar to that of HR^{6,10} and, when extracted carefully from the plant, without gel^{10,11} or short chain branching.^{9,11}

The present work analyzes the behavior of GR stored under accelerated conditions; the results are compared with those obtained for HR and CV Hevea rubber stored under the same conditions. In order to explain the results obtained with GR, the quantitative analysis of "abnormal" groups was carried out on the whole rubber and on fractions of different molecular weights.

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EXPERIMENTAL

Materials

Hevea Brasiliensis Rubber

The HR was obtained by coagulation from fresh latex collected in Tuxtepec, Oaxaca, Mexico. The coagulum was passed through a laboratory open mill to form sheets; these sheets were dried in a vacuum oven at room temperature. The same procedure was used for CV rubber stabilized⁵ with hydroxylamine hydrochloride (1.28 phr).

Guayule Rubber

GR from the pilot plant¹² in Saltillo, Mexico, was used for storage-hardening experiments. The sheets were prepared as mentioned previously.

Guayule Rubber Fractions

The rubber used for fractionation was obtained in the laboratory¹⁰ from plants with heights between 30 and 60 cm, and was exhaustively deresinated with acetone. The rubber was then dissolved in hexane and an anti-oxidant (250 ppm of 2,6 diterbutyl *p*-cresol) was added to the solvent. From this solution, fractions were precipitated by adding ethanol¹⁰ as a nonsolvent.

The molecular weight and polydispersity of the fractions were determined by gel permeation chromatography (GPC).

Storage Hardening

Samples of 250 g of dried rubber sheets were placed in a vacuum oven at 60°C with phosphorus pentoxide (P₂O₅) as a drying agent.⁵ From these sheets, samples for analysis of Mooney viscosity and molecular weight were taken every 12 hr.

Measurements

Mooney Viscosity

The Mooney viscosity of the stored samples was measured in a compact Monsanto Mooney viscometer (model C-1). The determinations were taken at 100°C using the large rotor, and the values noted 4 min after starting the test.

Molecular Weights

For molecular weight determinations a Waters Associates chromatograph (model GPC-200) with refractive index (RI) detector was used; the set for analytical columns consisted of 5 Styragel, 4 ft in length, $\frac{3}{8}$ in. o.d. columns, with a porosity of 10⁷, 10⁶, 10⁵, 10⁴, and 10³ Å. The solvent was tetrahydrofuran (THF) at 1 ml/min flow rate and a temperature of 30°C. Calibration (Fig. 1) was done with polystyrene standards and polyisoprene (Guayule fractions).

The universal calibration parameter (*J*) was used for calculations of molecular

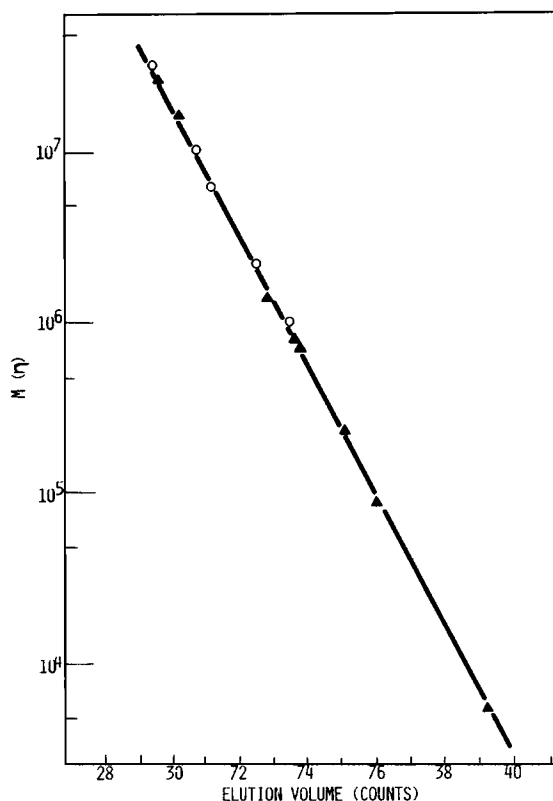


Fig. 1. GPC universal calibration curve using polystyrene standards and polyisoprene fractions (Guayule rubber fractions). (○) Polyisoprene; (▲) polystyrene.

weight averages, the Mark-Houwink constants used were those reported recently.¹⁰

Functional Groups Analysis

For quantitative analysis of functional groups in GR and GR fractions, the samples were dissolved in hexane-chlorobenzene (1:1 v/v) mixture and titrated with hydrogen bromide³ at different pH conditions in order to obtain the number of epoxy and/or amino groups. The titration technique was tested with synthetic polyisoprene (Ameripol), Guayule resin, and several amino acids (Table I).

RESULTS AND DISCUSSION

Storage Hardening

The relation between Mooney viscosity and accelerated storage time is shown in Figure 2 for the different samples analyzed.

The unstabilized HR shows an increment of 48 Mooney units after 48 storage hr; this is the expected behavior¹³ for this rubber. Hydroxylamine-treated CV rubber also shows the expected behavior because carbonyl groups are blocked by reaction with hydroxylamine⁵ and, therefore, the hardening reactions cannot occur and the Mooney viscosity remains constant.

TABLE I
Analysis of Functional Groups of Known Samples

Sample	Number of total functional groups (amino + epoxy)	Number of amino groups
Arginine	—	2.0
Ethylenediamine	—	2.3
Piperidine	—	1.1
Epoxol 7-4 ^a	4.1	—
Ameripol ^b	10.5 ^c	2.0
Guayule resin	0.0143 ^d	—

^a Epoxidized soybean oil (Swift Chemical Co.).

^b Synthetic polyisoprene.

^c Per chain of MW = 1×10^6 g/mole.

^d g HBr/g of resin.

GR shows unexpected results because, although this rubber was not treated with hydroxylamine, it keeps a constant Mooney viscosity. This fact suggests that this rubber does not have adequate properties to sustain crosslinking reactions. It was later concluded that this is due to the absence of functional reactive groups.

The GPC results (Fig. 3) confirmed the behavior of GR because its molecular weight is constant throughout the experiment and that of CV Hevea decreases a little but then remains constant. From these results, it is concluded that the fact that Mooney viscosity does not increase during the storage is not due to the degradation of the polymer.

For unstabilized Hevea, the molecular weight decreases as storage time increases; but, on the other hand, Mooney viscosity increases, showing that an inverse relationship exists between molecular weight and Mooney viscosity. This fact is very probably due to the formation of insoluble material,⁸ macro and micro gel, with very high Mooney viscosity which becomes the dominant factor in this parameter.

As solutions were filtered before injection to GPC, the gel was eliminated from

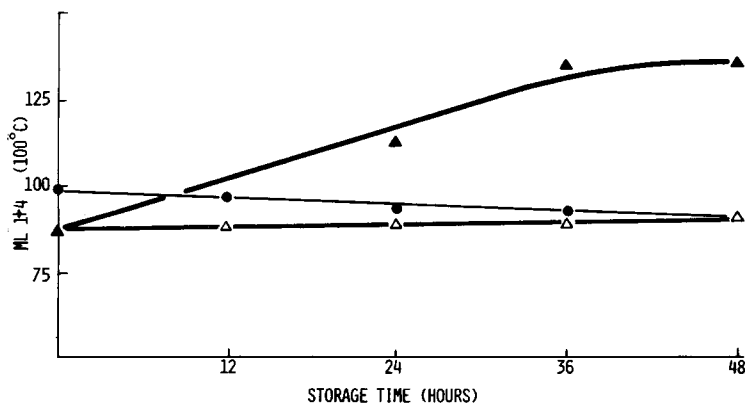


Fig. 2. Change of Mooney viscosity with storage time for different rubbers. Stabilized Hevea rubber treated with hydroxylamine hydrochloride (1.28 phr). (▲) Hevea unstabilized; (△) Hevea stabilized; (●) Guayule.

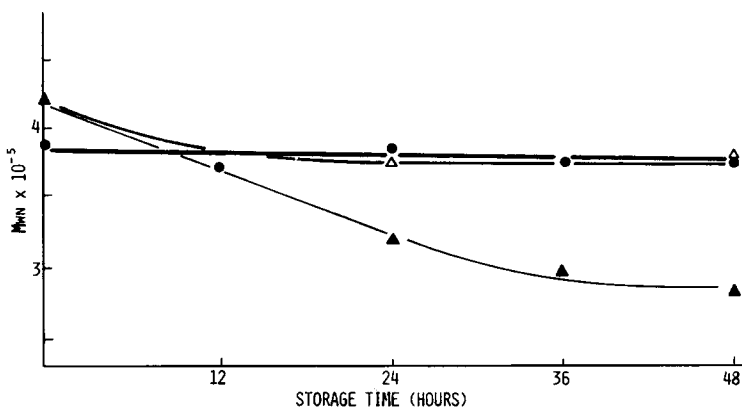


Fig. 3. Change of molecular weight (soluble fraction) for different rubbers. $\bar{M}_{wn} = (\bar{M}_w \cdot \bar{M}_n)^{1/2}$ data obtained from GPC calculations. Symbols as in Fig. 2

the samples and the results are those of the soluble fraction. However, they still show that crosslinking reactions stop in CV rubber and do not occur in GR, as molecular weight is constant throughout the experiment.

Functional Groups

The results of functional groups with known samples are shown in Table I; the value obtained for synthetic polyisoprene Ameripol (two amino groups in the chain) was unexpected because this sample is supposed to not have amino groups. This result could be due to the presence of a chemical entity³ that can react with the titrating agent, such as an anti-oxidant or other low-molecular-weight species, or to the technique; that is, the high molecular weight of the sample and the test is not sufficiently sensitive to determine whether there are two amino groups or none.

The arginine ($C_6H_8O_2N_4$) has four amino groups but only two are primary amines; the secondary amine ($-NH-$) and the imine ($=NH_2$) do not react.³

In Table I, it can be seen that Guayule resin reacts with the acid; and therefore, it is necessary to extract it from the rubber before titration. For this reason, GR was highly purified in order to eliminate all the impurities.

The quantitative analysis of functional groups in the highly purified rubber, titrated under nitrogen atmosphere and with anti-oxidant, gave a total of six groups in a chain of 1 million g/mole molecular weight. The number of functional groups was redetermined with the fractions; the variation of functional groups with molecular weight is shown in Figure 4. The 1×10^6 g/mole molecular weight sample showed a total of six groups, two of them being amino groups but, as mentioned before, this is equal to the rubber blank; and, therefore, it is possible to say that there could be no amino groups at all. The remaining four groups (epoxy) decrease with molecular weight reaching one at 6×10^5 g/mole, and could be due to the handling of the rubber.

These numbers, and the fact that GR does not undergo hardening during storage, strongly support the theory that there is not an adequate number of functional groups. A more sophisticated analysis technique, such as high resolution NMR or reactions with labeled substances, especially with low molecular

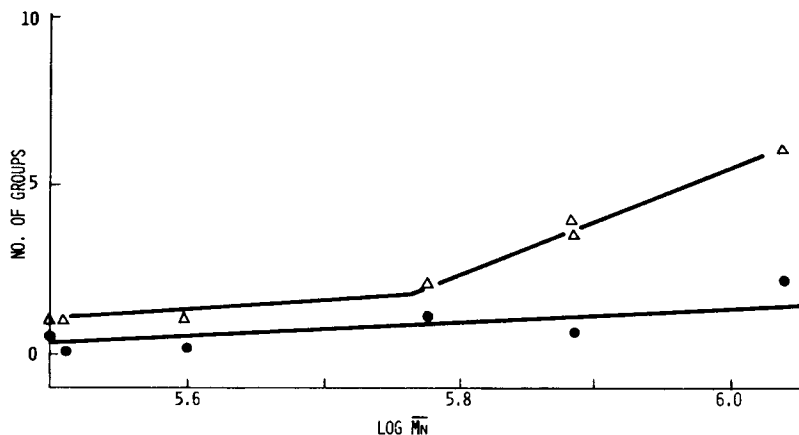


Fig. 4. Variation of functional "abnormal" groups in Guayule rubber fractions of different molecular weight (\bar{M}_n by GPC). (Δ) Amino plus epoxy groups; (●) amino groups.

weight fractions, could demonstrate whether there are one or two groups in the molecule.

CONCLUSIONS

The GR is a *cis* 1,4 polyisoprene that does not undergo storage hardening under dry accelerated storage conditions. This behavior is different from that observed in unstabilized HR, which becomes harder under these conditions, and is similar to that of CV rubbers.

It was found that the molecular weight average ($M_w M_n$)^{1/2} of the soluble fraction of unstabilized Hevea decreases during storage, possibly due to the formation of gel, and that of CV Hevea rubber (hydroxylamine treated) and GR is constant throughout the experiment. The ($M_w M_n$)^{1/2} was used because it is related both to molecular weight at the maximum of the peak and to MWD.¹⁴

The chemical analysis of "abnormal" groups in Guayule showed that the behavior of this rubber is due to the absence of reactive functional groups. Due to the sensitivity of the technique, and the high molecular weight of the samples, it is not possible to say whether the number of groups is zero or if there are one or two groups present in the chain; however, these are not enough to promote hardening during storage.

The fact that the high-molecular-weight sample has six "abnormal" groups could be due to the handling of the sample, as only the number of epoxy groups increases and at low molecular weight all the groups remain almost constant.

Previous results reported for HR fractions² show that the number of functional groups increases with molecular weight, starting with 26 groups ($\bar{M}_v \approx 1 \times 10^6$) and reaching over one hundred ($\bar{M}_v \approx 1 \times 10^6$).

The results obtained could indicate that there are differences in the biosynthetic processes of Guayule and *Hevea brasiliensis*. This is, at the moment, a speculative proposition and requires a deeper study on the biosynthetic characteristics of the plants to prove such differences.

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