

Effect of Iron Oxides on the Thermal Degradation of Natural Rubber from *Manihot glaziovii*

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SYNOPSIS

The effect of iron oxides particles mixed in natural rubber (NR) or aged natural rubber (ANR) from *Manihot glaziovii* were investigated. IR spectroscopy showed that α -Fe₂O₃ inhibits or retards the thermal degradation (200°C) of ANR, but it does not inhibit or retard the thermal degradation of NR. A retardation effect is observed using iron (III) oxide in both ANR and NR. Using both oxides, longer autoxidation induction periods of ANR and NR are observed (150°C). The periods were extended for a higher content of rubber hydroperoxide concentration. The inhibition or retardation of autoxidation using Fe₃O₄ in both ANR and NR is not evident. We suggest an interaction between hydroxyl groups of hydroperoxide, mainly present in aged natural rubber, and the iron oxide surface.

INTRODUCTION

Inorganic substances, that is, ions and oxides of transition metals, can act as catalysts or inhibitors of degradation in polymeric systems. Although the kinetics of oxidation processes catalyzed by metallic ions are not yet well understood, there is evidence that the metallic ion affects their initiation and propagation rates.^{1,2} The catalytic effects of the metallic compounds upon the aging and oxidation of polymers have been studied by Ranby and Rabeck.³ Some of the suggested possible reactions catalyzed by metals are:

1. $M^{(n+1)} + RH \rightarrow M^{n+} + \dot{R} + H^+$
2. $M^{(n+1)} + RCH_2OH \rightarrow M^{n+} + R\dot{C}HOH + H^+$
 $M^{(n+1)} + RCHO \rightarrow M^{(n+1)} + R\dot{C}=O + H^+$
3. $M^{n+} + ROOH \rightarrow M^{(n+1)+} + R\dot{O} + OH^-$
 $M^{(n+1)} + ROOH \rightarrow M^{n+} + R\dot{O}_2 + H^+$

In some cases, the metal acts as an antioxidant agent³:

4. $R\dot{O}_2 + M^{n+} \rightarrow RO_2^- + M^{(n+1)+}$ (peroxide radicals destruction)
5. $-\text{CH}_2\text{CH}_2\dot{\text{C}}\text{HCH}_2- + M^{(n+1)} \rightarrow$
 $-\text{CH}_2\text{CH}=\text{CHCH}_2- + \text{H}^+ + M^{n+}$

In all cases, the oxidation state of the metallic ion is changed. Mayo et al.⁴ observed that iron, cobalt, and manganese ions in low oxidation states exhibit a strong retardation effect on the degradation of poly(cis-1,4-isoprene). However, there are few reports concerning the effect of metallic ions upon the degradation of poly(isoprene) from natural sources.

In this article we carried out an investigation of the behavior of some iron oxides on the thermal degradation of aged or fresh natural rubber from *Manihot glaziovii*.

EXPERIMENTAL

Natural rubber from *Manihot glaziovii*, aged for 6 years (ANR) at room conditions (light, 30°C), was supplied by the Agrarian Science Center of the Federal University of Ceará. Fresh natural rubber (NR) from *Manihot glaziovii* was a gift of Professor M. Cunha Filho from the Federal University of Ceará. It was naturally coagulated from latex and kept in

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Table I Iron Oxide Characteristics

Oxide Designation	Source ^{6,7}	Diameter Particle Size (Å)*	Description
α -Fe ₂ O ₃	Synthesis	≥ 180	Brown, antiferromagnetic
Iron (III) Oxide Fe ₃ O ₄	Oxidation of Fe(CO) ₅	≥ 180 and 180–100	Brown red, ferrimagnetic
	Synthesis	—	Black, ferrimagnetic

* The diameter particle size of the iron oxides was estimated roughly by the Mössbauer measurements and according to Kündig et al.⁸

the dark at 18°C. Both were purified following the method described previously⁵ by solubilization in chloroform and precipitation with ethanol. After filtering this mixture, the rubber was dried under vacuum at room temperature. The materials were characterized by their IR spectra. The iron oxides used, and their descriptions, are listed in Table I.

Films of both ANR and NR (thickness range: 40–70 μm) were cast onto PTFE by slow evaporation of aliquots of rubber solution containing 2 wt % of oxide particles. They were heated at 150°C or 200°C for different periods of time ranging from 5 to 120 min, at room atmosphere. The IR spectra were obtained using a Perkin-Elmer spectrophotometer, Model 283, with a PTFE film in the reference beam.

Mössbauer spectra were obtained at room temperature, using a Co (Rh) source in a conventional constant acceleration spectrometer, operating in transmission geometry mode. Mössbauer parameters

were determined by computer fitting, using a least-square routine. The Mössbauer samples had an effective thickness of 5 mg/cm². The isomer shifts (IS) shown are relative to metallic iron.

RESULTS

Aged Natural Rubber (ANR) and Natural Rubber (NR) Films Containing α -Fe₂O₃ Particles

Figure 1 shows the IR spectra of ANR and NR films, containing 2 wt % α -Fe₂O₃, before and after heating (200°C for 5 min). The spectra show peaks at PTFE absorption regions (2500–2200 cm⁻¹, 1300–1100 cm⁻¹, and 800–500 cm⁻¹) due to experimental problems related to the unevenness of the PTFE film thickness. However, those peaks did not affect the characteristic rubber absorption regions (1665 cm⁻¹,

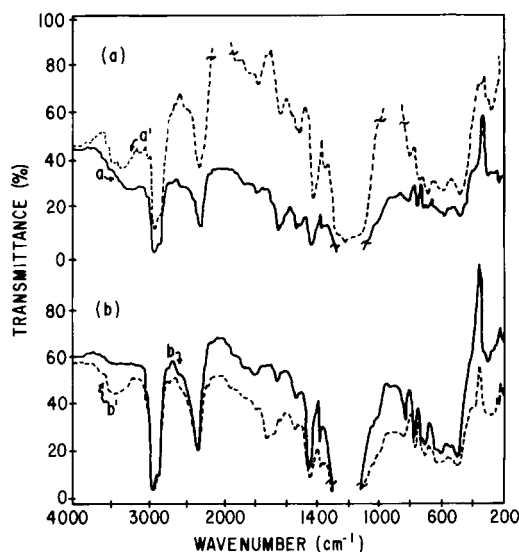


Figure 1 IR spectra of ANR and NR films with 2 wt % α -Fe₂O₃. (a, b) before heating; (a', b') after heating for 5 min at 200°C.

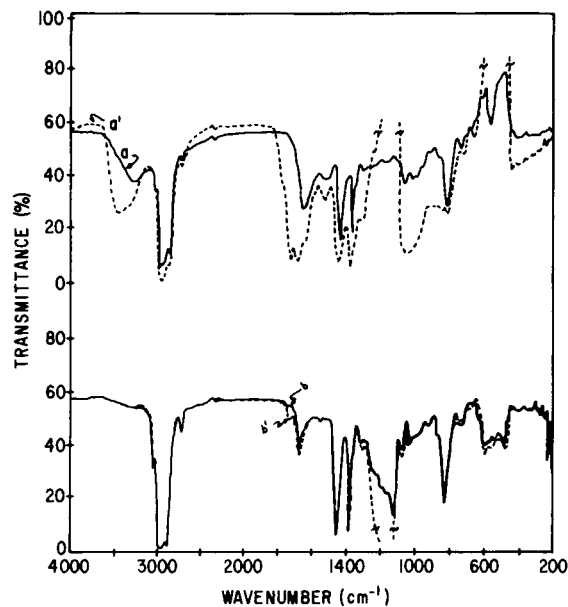


Figure 2 IR spectra of ANR and NR films. (a) ANR; (B) NR; (a, b) before heating; (a', b') after heating for 5 min at 200°C.

$\nu\text{C}=\text{C}$; 840 cm^{-1} , $\delta\text{C}=\text{C}$). The IR spectra of films of ANR with 2 wt % $\alpha\text{-Fe}_2\text{O}_3$ are essentially the same before and after heating (200°C , 5 min), indicating no change due to oxidation in the absorption region of carbonyl groups (1720 cm^{-1} , $\nu\text{C}=\text{O}$) or hydroxyl groups ($3500\text{--}3300\text{ cm}^{-1}$); see Figure 1 (a, a'). The spectra of NR film with 2 wt % $\alpha\text{-Fe}_2\text{O}_3$, before and after heating, are shown in Figure 1 (b, b'). In this case, carbonyl and hydroxyl peaks can be seen after heating (200°C , 5 min) at 1720 cm^{-1} ($\nu\text{C}=\text{O}$) and 3500 cm^{-1} (νOH). So, the presence of $\alpha\text{-Fe}_2\text{O}_3$ in the NR does not inhibit the oxidation previously observed on pure NR under the same thermal treatment conditions (Fig. 2b). This differs essentially from the thermal behavior observed for ANR (Fig. 2a).

The Mössbauer spectra of the films of ANR and NR, containing 2 wt % $\alpha\text{-Fe}_2\text{O}_3$, were run before and after heating (200°C , 5 min) (Figs. 3 and 4). They were fitted as sextets and their shape and Mössbauer parameters did not change due to heating. Both isomer shift (IS) and quadrupole splitting (ΔE_Q) values, shown in Table II, fall in the range characteristic of antiferromagnetic $\alpha\text{-Fe}_2\text{O}_3$. In this case, the iron environment in the iron oxide remains

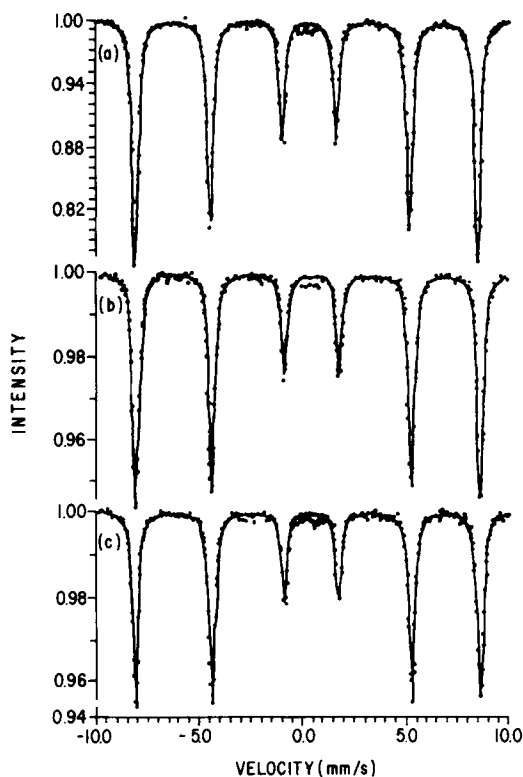


Figure 3 Mössbauer spectra. (a) $\alpha\text{-Fe}_2\text{O}_3$; (b) ANR + $\alpha\text{-Fe}_2\text{O}_3$; (c) NR + $\alpha\text{-Fe}_2\text{O}_3$.

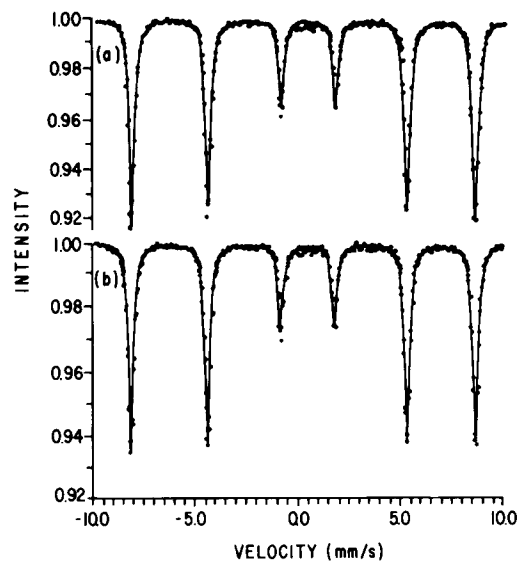


Figure 4 Room temperature Mössbauer spectra of samples heated for 5 min at 200°C . (a) $\alpha\text{-Fe}_2\text{O}_3$; (b) ANR + $\alpha\text{-Fe}_2\text{O}_3$; (c) NR + $\alpha\text{-Fe}_2\text{O}_3$.

unaltered after thermal treatment of both ANR and NR. The ratio between the intensities of the first and the second lines of the sextet spectra of both ANR + $\alpha\text{-Fe}_2\text{O}_3$ and NR + $\alpha\text{-Fe}_2\text{O}_3$ decrease as compared to the same ratio for the pure $\alpha\text{-Fe}_2\text{O}_3$ spectrum (Fig. 3). This characterizes a surface ordering of $\alpha\text{-Fe}_2\text{O}_3$ into the rubber matrix.

Aged Natural Rubber (ANR) and Natural Rubber (NR) Films Containing Iron (III) Oxide Particles

The IR spectra of ANR films with 2 wt % iron (III) oxide are shown in Figure 5. The same difficulties were noted with respect to spectrum compensation on the reference beam. However, it was observed on the unaffected absorption regions that the spectra of ANR did not change after heating for 5 min at 200°C ; see Figure 5 (a, a'). Also, the IR spectrum of NR after heating (Fig. 5b') does not show the presence of peaks due to oxidation (1720 cm^{-1} , $\nu\text{C}=\text{O}$ and 3500 cm^{-1} , νOH). A peak at 3300 cm^{-1} in the spectra of NR, before and after heating, not present in the original NR spectrum, was interpreted as being due to νOH from oxide structure; see Figure 5 (b, b'). This suggests that the iron (III) oxide retards or inhibits the oxidation process on ANR and NR. The Mössbauer spectra of ANR + 2 wt % iron (III) oxide did not change with heating. They were fitted as the superposition of a sextet and an asymmetric doublet (Fig. 6). Mössbauer parameter values were IS = 0.26 mm/s and $\Delta E_Q = 0.19\text{ mm/s}$ for the sextet, and IS = 0.35 mm/s and $\Delta E_Q = 0.86$

Table II Room Temperature Mössbauer Parameters

Sample	Spectrum	IS* (mm/s)	Δ EQ (mm/s)	H [†] (kG)
ANR + α -Fe ₂ O ₃	6 Lines	0.26 ± 0.01	0.20 ± 0.01	520 ± 3
ANR + α -Fe ₂ O ₃ (200°C, 5 min)	6 Lines	0.26 ± 0.01	0.23 ± 0.01	521 ± 3
NR + α -Fe ₂ O ₃	6 Lines	0.25 ± 0.01	0.22 ± 0.01	522 ± 3
NR + α -Fe ₂ O ₃ (200°C, 5 min)	6 Lines	0.27 ± 0.01	0.21 ± 0.01	522 ± 3
α -Fe ₂ O ₃	6 Lines	0.24 ± 0.01	0.22 ± 0.01	517 ± 3

* IS is relative to metallic iron.

† Hyperfine magnetic field.

mm/s for the doublet (Table III). The IS values are characteristic of iron (III) nuclei (high spin). The doublet was interpreted as being due to superparamagnetic α -Fe₂O₃ particles and the sextet as being due to hydrated iron oxide particles with the probable structure of δ -FeOOH as confirmed by its synthesis, its IR spectrum and its magnetic properties.⁹ The Mössbauer spectra of NR with 2 wt % iron (III) oxide particles showed the same pattern as those for ANR.

Induction Periods of Autoxidation of Aged Natural Rubber (ANR) and Natural Rubber (NR) at 150°C

Figure 7 shows the peak intensity ratio ($\nu_{C=O}/\delta_{C=C}$) from IR spectra of ANR and NR films containing 2 wt % of either α -Fe₂O₃, iron (III) oxide or Fe₃O₄, heated for 0, 5, 10, 15, 30, 60, and 90 min, at 150°C.

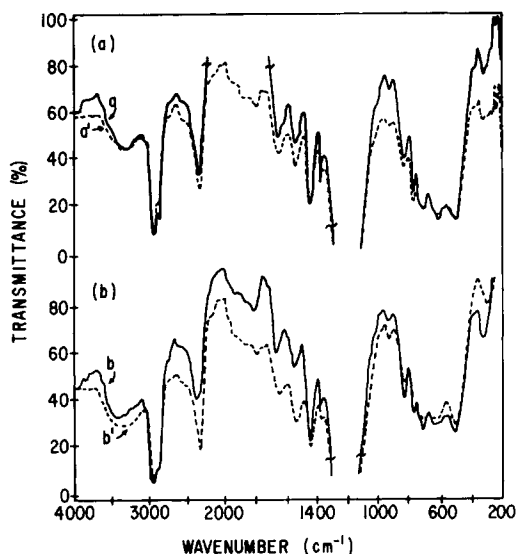


Figure 5 IR spectra of ANR and NR films with 2 wt % iron (III) oxide. (a) ANR; (b) NR; (a, b) before heating; (a', b') after heating for 5 min at 200°C.

An induction period of 15 min was observed in pure ANR. A longer induction period (30 min) was observed in both ANR + 2 wt % α -Fe₂O₃ and ANR + 2 wt % iron (III) oxide films. No effect on the induction period was observed using Fe₃O₄ (Fig. 7a).

An induction period of 5 min was observed in pure NR and a longer induction period was found in NR with 2 wt % α -Fe₂O₃ or iron (III) oxide particles (15 min) or Fe₃O₄ particles (10 min); see Figure 7(b). The inhibition effect on the autoxidation of rubber, observed using α -Fe₂O₃ and iron (III) oxide, is more evident in the ANR. The Fe₃O₄ does not affect strongly the autoxidation of rubber.

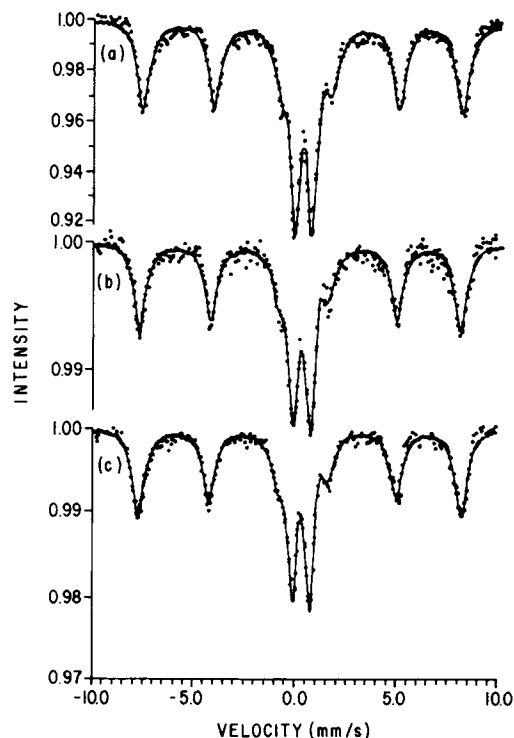


Figure 6 Room temperature Mössbauer spectra. (a) Iron (III) oxide; (b) ANR + iron (III) oxide; (c) ANR + iron (III) oxide after heating for 5 min at 200°C.

Table III Room Temperature Mössbauer Parameters

Sample	Spectrum	IS* (mm/s)	ΔEQ (mm/s)	H [†] (kG)
ANR + Iron (III) Oxide	Asymmetric Doublet	0.35 ± 0.01	0.86 ± 0.01	490 ± 3
	6 Lines	0.26 ± 0.01	0.19 ± 0.01	
ANR + Iron (III) Oxide (200°C, 5 min)	Asymmetric Doublet	0.34 ± 0.01	0.85 ± 0.01	—
	6 Lines	0.29 ± 0.01	0.17 ± 0.01	492 ± 3
Iron (III) Oxide	Asymmetric Doublet	0.34 ± 0.01	0.85 ± 0.01	—
	6 Lines	0.25 ± 0.01	0.17 ± 0.01	491 ± 3

* IS relative to metallic iron.

† H = Hyperfine magnetic field.

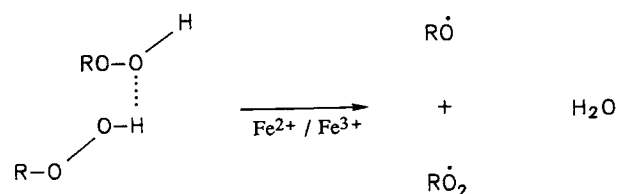
DISCUSSION

The iron ions in metallic complexes are reversibly oxidized and reduced by hydroperoxide yielding free radicals and acting as a catalyst for degradation of polymeric systems¹:



The total effect in such processes is the reduction of the activation energy of the initiation step for the

autoxidation reaction, keeping unaltered the oxidation rate.



However, it was observed in this work, that iron as oxide can also act as an inhibitor of the autoxidation process of natural rubber from *Manihot glaziovii* with a longer induction period observed with the aged rubber (ANR). On the other hand, ⁵⁷Fe Mössbauer spectra showed no changes in either the charge symmetry or the electron density surrounding the iron nuclei on the two types of iron oxide added to the rubber, before or after thermal treatment of the samples. We suggest an interaction between hydroxyl groups of hydroperoxide, mainly present in aged natural rubber, and the iron oxide surface inhibiting the initiation step of the autoxidation reaction. This initiation occurs mainly by hydroperoxide decomposition

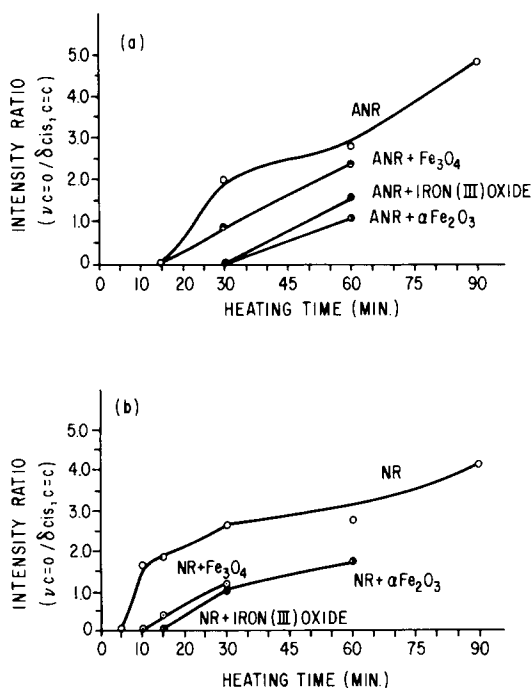
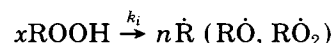
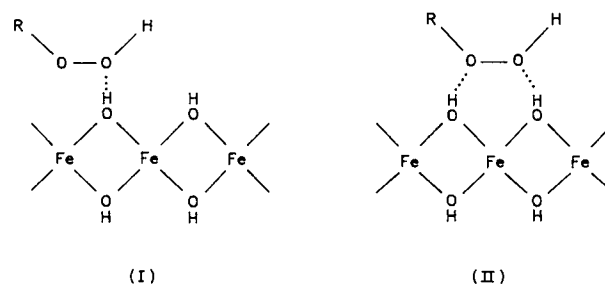


Figure 7 Peak intensity ratio ($\delta_{C=O}/\delta_{C-C}$) from IR spectra of ANR and NR films. (a) ANR; (b) NR; Temperature 150°C.



The interaction models we propose are shown below:



The inhibition of autoxidation of ANR and NR by Fe_3O_4 was not as effective, perhaps due to a competition between the inhibition and the catalytic process by electron transfer.¹

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