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## DEPOLYMERIZATION OF NATURAL RUBBER LATEX USING PHENYLHYDRAZINE- $\text{FeCl}_2$ SYSTEM

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### ABSTRACT

Natural rubber latex was depolymerized by a phenylhydrazine-ferrous chloride system. The influence of phenylhydrazine, ferrous chloride, and ferric chloride at initial pH values of 7 and 10 on degree of depolymerization was investigated. The conversion from ferrous ion to ferric ion and vice versa, the consumption of phenylhydrazine, and the formation of radicals initiating the decomposition process have been suggested.

Among the complications that can lower the solubility and the activity of natural rubber (*cis*-1,4-polyisoprene) is its high molecular weight polymer chain. Several workers have tried to depolymerize the polyisoprene chain by phenylhydrazine-oxygen systems [1–4]. S. Yamashita and coworkers have investigated the degradation of *cis*-1,4-polyisoprene in benzene by the  $\text{PhNHNH}_2$ - $\text{FeCl}_2$  system [5–10]. From the obtained results, they suggested that:

- The degree of degradation increases rapidly when the reaction is carried out in the presence of  $\text{PhNHNH}_2$  and  $\text{FeCl}_2$ , but mainly depends on the amount of used  $\text{PhNHNH}_2$ .
- The reaction of  $\text{PhNHNH}_2$  with  $\text{FeCl}_2$  in benzene solution (under  $\text{N}_2$  atmosphere) rapidly produced a 2:1 complex, which rapidly decomposed in the presence of oxygen to yield radicals initiating depolymerization.



TABLE 1. Degree of Depolymerization Depends on the Content of  $\text{FeCl}_2$  at  $\text{pH}_0$  7

	Run							
	1a	1b	1c	1d	1e	1f	1g	1h
PhNHNH <sub>2</sub> (mmol)	1.2	1.2	1.2	1.2	1.2	1.2	0.6	0.6
FeCl <sub>2</sub> (mmol)	0.01	0.02	0.045	0.055	0.15	0.3	0.0	0.3
	[ $\eta$ ] (dL/g)							
Time (min)								
5	0.69	0.56	0.40	0.40	0.40	0.40	2.97	0.64
30	0.61	0.54	0.39	0.40	0.40	0.40	2.94	0.62
120	0.60	0.51	0.39	0.39	0.39	0.39	2.94	0.60

*Note.* 60% natural rubber latex = 10 g; lauryl sulfate = 0.3 g;  $T = 30^\circ\text{C}$ ; speed of stirring = 400 rpm.

The degree of degradation was found independent of the amount of  $\text{FeCl}_2 > 0.045$  mmol.

At higher  $\text{pH}_0$  10 (Table 2), the degradation became slower at the beginning of the reaction due to the slow decomposition of the complex in the high  $\text{pH}_0$  medium. This period can be accelerated by raising the amount of  $\text{FeCl}_2$  (formation of hydroxo of ionic ion, which lowers the pH of the medium, Table 3).

TABLE 2. Degree of Polymerization Depends on the Content of  $\text{FeCl}_2$  at  $\text{pH}_0$  10

	Run			
	2a	2b	2c	2d
PhNHNH <sub>2</sub> (mmol)	0.6	0.6	0.6	0.6
FeCl <sub>2</sub> (mmol)	0.3	0.6	1.2	3.0
	[ $\eta$ ] (dL/g)			
Time (min)				
5	1.24	—	0.99	0.70
15	1.13	1.00	0.92	—
30	—	—	0.83	0.56
120	0.80	0.69	0.64	Gel

*Note.* 60% natural rubber latex = 10 g; lauryl sulfate = 0.3 g;  $T = 30^\circ\text{C}$ ; speed of stirring = 400 rpm.

TABLE 3. Influence of FeCl<sub>2</sub> on pH<sup>a</sup> of the Reaction Medium with Respect to Time

Run	FeCl <sub>2</sub> (mmol)	Time (min)					
		0	1	5	15	30	60
3a	0.3	10	—	8.7	8.7	8.7	8.7
3b	1.2	10	8.1	8.0	7.7	7.6	7.6
3c	3.0	10	6.8	6.8	6.8	6.7	6.6
3d	0.3	7	6.4	6.3	—	—	6.1

Note. 60% natural rubber latex = 10 g; lauryl sulfate = 0.3 g;  $T = 30^{\circ}\text{C}$ ; PhNHNH<sub>2</sub> = 0.6 mmol.

<sup>a</sup>Measured by pH meter.

TABLE 4. Influence of PhNHNH<sub>2</sub> on Degradation of Natural Rubber Latex at pH<sub>0</sub> 7

	Run				
	4a	4b	4c	4d	4e
PhNHNH <sub>2</sub> (mmol)	0.6	1.2	1.5	1.8	2.4
FeCl <sub>2</sub> (mmol)	0.3	0.3	0.3	0.3	0.3
	[ $\eta$ ] (dL/g)				
Time (min)					
5	0.64	0.40	0.35	0.33	0.30
30	0.62	0.40	0.33	0.31	0.27
120	0.60	0.39	0.31	0.29	0.27

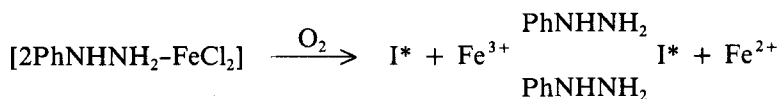
Note. 60% natural rubber latex = 10 g; lauryl sulfate = 0.3 g;  $T = 30^{\circ}\text{C}$ ; speed of stirring = 400 rpm.

### Influence of PhNHNH<sub>2</sub>

The increase in the degree of degradation with the amount of PhNHNH<sub>2</sub> was visible at both pH<sub>0</sub> values (Tables 4 and 5). This indicates that PhNHNH<sub>2</sub> plays the principal part in the redox system regardless of whether FeCl<sub>2</sub> or FeCl<sub>3</sub> is used.

### Influence of FeCl<sub>2</sub> and FeCl<sub>3</sub>

When FeCl<sub>3</sub> was used instead of FeCl<sub>2</sub> the rate of decomposition also considerably increased (but at the beginning of the reaction, the rate was slower in comparison with the use of FeCl<sub>2</sub>). Therefore FeCl<sub>3</sub> plays the same role with FeCl<sub>2</sub> (Table 6). Thus, the initiation of depolymerization may be described as follows:



where  $\text{I}^*$  = radical.

TABLE 5. Influence of  $\text{PhNHNH}_2$  on Degree of Depolymerization of Natural Rubber Latex at  $\text{pH}_0$  10

	Run				
	5a	5b	5c	5d	5e
$\text{PhNHNH}_2$ (mmol)	0.6	1.2	1.5	1.8	2.4
$\text{FeCl}_2$ (mmol)	0.3	0.3	0.3	0.3	0.3
	[ $\eta$ ] (dL/g)				
Time (min)					
5	1.24	0.53	0.48	0.40	0.41
15	1.13	0.46	—	—	0.32
30	—	0.44	0.39	0.33	0.29
60	0.85	0.43	—	—	0.28
120	0.80	0.41	0.35	0.32	0.28

Note. 60% natural rubber latex = 10 g; lauryl sulfate = 0.3 g;  $T = 30^\circ\text{C}$ ; speed of stirring = 400 rpm.

TABLE 6. Comparison of Degree of Degradation of Natural Rubber Latex Using the  $\text{PhNHNH}_2\text{-FeCl}_2$  and the  $\text{PhNHNH}_2\text{-FeCl}_3$  System

	Run				
	4b	6a	5b	6b	6c
$\text{PhNHNH}_2$ (mmol)	1.2	1.2	1.2	1.2	1.2
$\text{FeCl}_2$ (mmol)	0.3	—	0.3	—	—
$\text{FeCl}_3$ (mmol)	—	0.3	—	0.3	0.075
$\text{pH}_0$	7	7	10	10	7
	[ $\eta$ ] (dL/g)				
Time (min)					
5	0.40	0.46	0.53	0.90	0.46
120	0.39	0.39	0.41	0.66	0.39

Note. 60% natural rubber latex = 10 g; lauryl sulfate = 0.3 g;  $T = 30^\circ\text{C}$ ; speed of stirring = 400 rpm.

The complex formed from  $\text{FeCl}_2$  and  $\text{PhNHNH}_2$  is readily decomposed under air or oxygen atmosphere to yield  $\text{Fe}^{3+}$  and radicals as well as related reactive species ( $\text{I}^*$ ) causing the degradation. This ion is then combined with the excess of  $\text{PhNHNH}_2$  forming an active complex that is again decomposed to yield radicals and  $\text{Fe}^{2+}$ . The cycle is continued until  $\text{PhNHNH}_2$  is totally consumed.

### Analysis of the Products Obtained from the Reaction of $\text{PhNHNH}_2$ with $\text{FeCl}_2$ Without Polymer Molecules

Gas chromatographic analysis of the reaction mixture shows the presence of benzene, phenol, and biphenyl. The overall amount of products yielded from decomposition of the  $\text{PhNHNH}_2\text{-FeCl}_3$  mixture is less than that obtained with  $\text{PhNHNH}_2\text{-FeCl}_2$ . In addition, the overall amount of products obtained from the decomposition of the  $\text{PhNHNH}_2\text{-FeCl}_2$  mixture at  $\text{pH}_0$  7 is greater than the value at  $\text{pH}_0$  10. The results are shown in Table 7.

### IR Spectrum Analysis

Along with the specific peaks of *cis*-1,4-polyisoprene, there are peaks at 3292 and  $1700\text{ cm}^{-1}$  (COOH);  $1722\text{ cm}^{-1}$  (aldehyde); and 1640 and  $700\text{ cm}^{-1}$  indicating C=N and phenylhydrazone.

### $^1\text{H-NMR}$ Spectrum Analysis

The additional peak at  $\delta = 1.25$  ppm (weak) indicating ternary proton ( $-\text{C}-\text{H}$ ) shows that there is crosslinking between macroradicals (at  $\text{C}\alpha$ -methylene). The strength of this peak increases when the degree of depolymerization increases; this can also be seen from the higher values of  $M_w/M_n$  (Table 8) (the higher dispersion of molecular weight):

TABLE 7. Results of Gas Chromatographic Analysis of the Products Obtained by Mixing  $\text{PhNHNH}_2$  and  $\text{FeCl}_2$  (or  $\text{FeCl}_3$ ) Without Rubber

$\text{pH}_0$	$\text{PhNHNH}_2$ (mmol)	$\text{FeCl}_2$ (mmol)	$\text{FeCl}_3$ (mmol)	Ether-soluble products (mmol)		
				Benzene	Phenol	Biphenyl
7	1.2	0.6	—	0.064	0.045	$4.34 \times 10^{-3}$
10	1.2	0.6	—	0.042	0.044	0
7	2.4	0.6	—	0.096	0.043	$6.14 \times 10^{-3}$
7	3.0	0.6	—	0.180	0.034	$8.17 \times 10^{-3}$
7	2.4	—	0.6	0.060	0.054	$4.2 \times 10^{-3}$

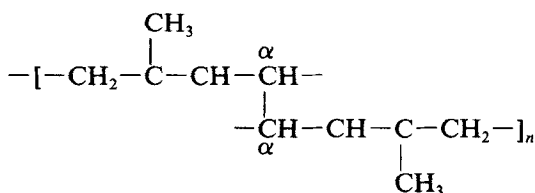
Note. Mixing time: 10 min.

TABLE 8. Values of  $M_n$ ,  $M_w$ , and  $M_w/M_n$  Were Obtained from GPC of Degraded Natural Rubber

$[\eta]^a$	$M_n$	$M_w$	$M_w/M_n$
0.72	16550	93566	5.65
0.45	10689	64300	6.01
0.40	8117	55520	6.84
0.27	2725	42223	15.49

Note. Solvent THF (debit 1 mL/min); PL gel ( $5m \times 4$ ):  $10^2$ ,  $5 \times 10^2$ ,  $10^4$ ,  $10^6$  Å; detector FID.

<sup>a</sup>Measured by Ostwald viscometer, solvent: toluene, at 30°C.



Based on the obtained results, the depolymerization can be carried out satisfactorily using 0.3 mmol of  $\text{FeCl}_2$  at  $\text{pH}_0$  10 and 0.045 mmol at  $\text{pH}_0$  7 (per 10 g of 60% NR latex) and  $> 1.2$  mmol of  $\text{PhNHNH}_2$  (depending on the desired degree of degradation).

## CONCLUSION

The degradation of natural rubber latex by  $\text{PhNHNH}_2\text{-FeCl}_2$  was investigated at  $\text{pH}_0 = 7$  and 10. The obtained results suggest  $\text{PhNHNH}_2$ ,  $\text{Fe}^{2+}$ , and  $\text{Fe}^{3+}$  have a role in the initiation process. By this system, LNR can be produced from NR latex in the appropriate conditions (at RT, short reaction time).

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