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STUDY OF THE CHEMICAL DEGRADATION OF NATURAL RUBBER AND SYNTHETIC *CIS*-1,4-POLYISOPRENE BY PHENYLHYDRAZINE-IRON (II) CHLORIDE SYSTEM USING GEL PERMEATION CHROMATOGRAPHY

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Abstract

Degradation of cis-*1, 4-polyisoprene and natural rubber by phenylhydrazine-iron (II) chloride system were investigated in tetrahydrofuran solution at 30°C in the opened container. Gel permeation chromatography was used to follow the reactions. It was found that the number-average molecular weight of the rubbers were reduced to nearly one-half in the first few hours and the shape of the molecular weight distribution curves was essentially unchanged.*

The degradative reactions of vulcanized and unvulcanized 1, 4-polyisoprene and various synthetic rubbers by phenylhydrazine-iron (II) chloride system under various conditions have been elucidated by S. Yamashita *et al.*[1-3]. The reactions were carried out in benzene solution and changes in the molecular weight were followed from viscosity measurements. The aim of the study was to find a suitable reagent and conditions for the reclamation of synthetic rubber vulcanisates. In the present work the degradation of unvulcanized natural rubber and *cis*-1, 4-polyisoprene rubber, using the same reagent at a choosen condition, were carried out in tetrahydrofuran solution. Gel permeation chromatography was used to follow the extent of degradation and the change in molecular weight distribution.

Cis-1, 4-polyisoprene, IR-2200, provided by Japan Synthetic Rubber Co-Ltd., was masticated at room temperature for 20 min. The masticated rubber was purified twice by dissolving in benzene and then precipitated by pouring the benzene solution into excess methanol. The precipitate was dried under vacuum at room temperature. Natural rubber RSS-1 was masticated at room temperature for 20 min. and used without reprecipitation. Phenylhydrazine and iron (II) chloride were purchased from WAKO Pure Chemical Industries (extrapure grade). From thermogravimetric analysis iron (II) chloride contained 37.9% of water. Tetrahydrofuran was refluxed over sodium wire for a few hours, then distilled.

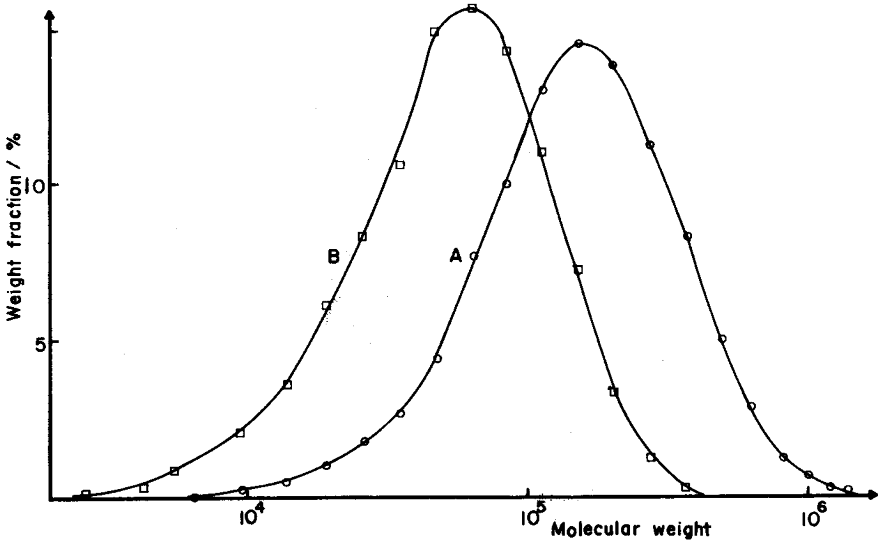

Fig. 1. Molecular weight distribution curves of *cis*-1, 4-polyisoprene reacted with phenylhydrazine-iron (II) chloride in tetrahydrofuran solution at 30 ° C at the reaction time

curve A : 15 min.
curve B : 25 hours

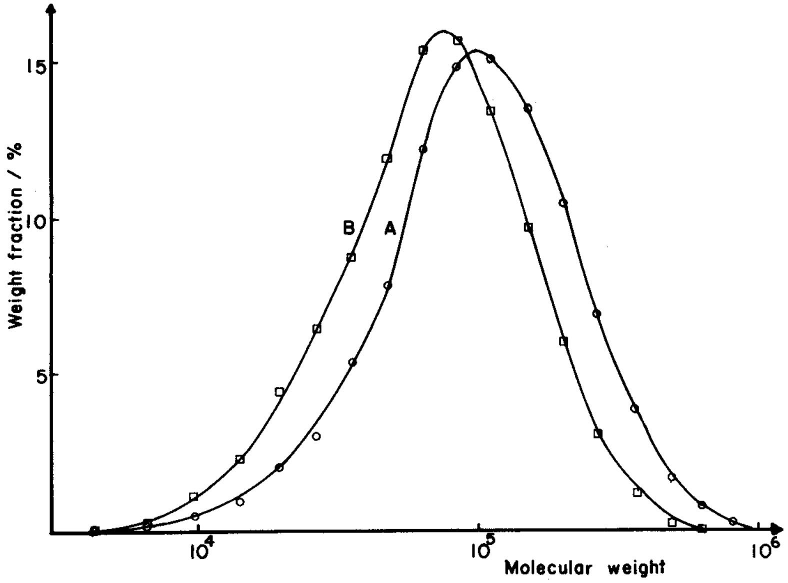

Fig. 2. Molecular weight distribution curves of natural rubber reacted with phenylhydrazine-iron (II) chloride in tetrahydrofuran solution at 30 ° C at the reaction time.

curve A : 15 min.
curve B : 24.5 hours

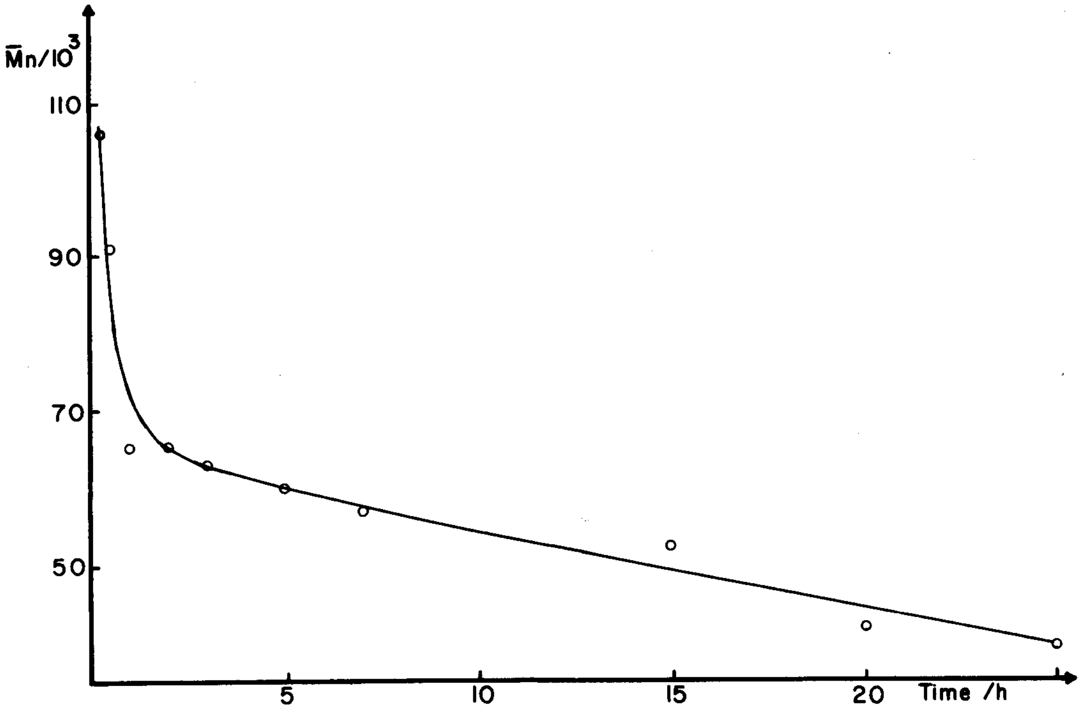

Fig. 3. Plot of $\overline{M}_n$ of cis-1, 4-polyisoprene v.s. time of degradative reaction.

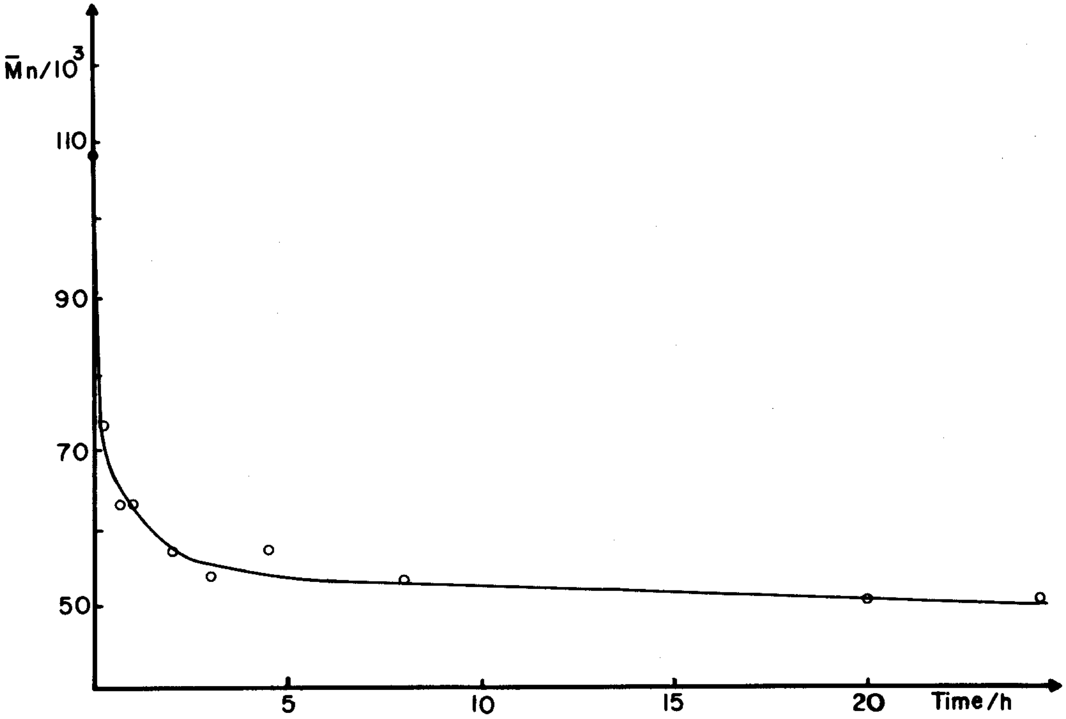

Fig. 4. Plot of $\overline{M}_n$ of natural rubber v.s. time of degradative reaction

TABLE 1 DATA ANALYSED FROM GPC MEASUREMENTS OF *CIS*-1, 4-POLYISOPENE REACTED WITH PHENYLHYDRAZINE-IRON (II) CHLORIDE SYSTEM. ($\overline{M}_n$ = NUMBER-AVERAGE, $\overline{M}_w$ = WEIGHT-AVERAGE MOLECULAR WEIGHT)

Reaction time (h)	$\overline{M}_n/10^3$	$\overline{M}_w/10^3$	$\overline{M}_w/\overline{M}_n$
0.25	106.3	210.1	2.0
0.5	91.2	202.4	2.2
1.0	65.4	150.9	2.3
2.0	65.7	143.2	2.2
3.0	63.3	141.0	2.2
5.0	60.0	131.7	2.2
7.0	57.6	119.5	2.0
15.0	51.7	107.8	2.0
20.0	42.6	82.5	1.9
25.0	39.6	72.0	1.8

TABLE 2 DATA ANALYSED FROM GPC MEASUREMENTS OF NATURAL RUBBER REACTED WITH PHENYLHYDRAZINE-IRON (II) CHLORIDE SYSTEM

Reaction time (h)	$\overline{M}_n/10^3$	$\overline{M}_w/10^3$	$\overline{M}_w/\overline{M}_n$
0	108.5	213.6	2.0
0.25	73.5	135.3	1.8
0.66	63.1	121.7	1.9
1.0	63.1	120.7	1.9
2.0	57.4	114.8	2.0
3.0	54.2	109.0	2.0
4.5	57.5	111.9	1.9
8.0	53.6	102.1	1.9
20.5	50.9	95.8	1.9
24.5	51.5	91.4	1.8

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Degradation of rubbers was carried out in a 250 ml three-necked flask which was thermostated at 30°C and stirred at constant rate of 100 rpm with a sealed stirrer. The oxygen supply for the reaction was merely from the air above the reaction mixture from the open-ended condensor.

About 1 g of masticated rubber (synthetic cis-1, 4-polyisoprene or natural rubber) was dissolved in 94 ml tetrahydrofuran in the reaction flask at 30°C. At constant 100 rpm stirring, 4 ml solution of 2.2 m mol phenylhydrazine in tetrahydrofuran was introduced into the rubber solution, then 0.2 m mol of powdered iron (II) chloride was added. The time at which addition of the latter reagent was made was taken as the starting time of the reaction. Two ml of the reaction mixture was removed at different time intervals, diluted with 8 ml of tetrahydrofuran, and injected into a gel permeation chromatograph (GPC; High speed liquid chromatograph HLC-802 UR, Toyo Soda Co.; TSK-Gel H-type GMH, 7.5 mm ID x 600 mm). Since each sample requires about 30 min for the GPC measurement, the first few samples were kept in the refrigerator prior to the measurements.

The data obtained from GPC were evaluated by a computer to give the number-average molecular weight ($\overline{M}_n$), weight-average molecular weight ($\overline{M}_w$), and $\overline{M}_w/\overline{M}_n$ ratio. Plots of molecular weight distribution of synthetic cis-1, 4-polyisoprene and natural rubber after the degradation reaction took place for 15 min. and 25 hours are shown in Figs. 1 and 2 respectively. As the reaction proceeded the number-average molecular weight of the two rubbers decreased as shown in Figs. 3 and 4. The numerical of $\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ of the two rubbers at various reaction times are listed in Tables 1 and 2.

From Figs. 3 and 4, together with numerical values given in Tables 1, and 2, it can be seen that the number-average molecular weight of the rubbers decreased rapidly in the first few hours of the reaction. In 25 hours, $\overline{M}_n$ of both natural and synthetic rubbers were reduced to about one-half. For all reaction times, the ratio $\overline{M}_w/\overline{M}_n$ remains almost constant at 2.0 (see Tables 1 and 2). This means that the polydispersity of the polymers is nearly constant during the degradation. This can also be seen from the shape of the molecular weight distribution curves shown in Figs. 1 and 2.

Acknowledgements

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บทคัดย่อ

จากการศึกษาปฏิกิริยาสลายโมเลกุลของยางสังเคราะห์ cis-1, 4-polyisoprene และยางธรรมชาติโดยใช้ phenylhydrazine-Iron (II) chloride ในตัวทำละลาย tetrahydrofuran ที่ 30°C ในภาชนะเปิด, ติดตามการเปลี่ยนแปลงของน้ำหนักโมเลกุลโดยใช้ Gel Permeation Chromatography พบว่า น้ำหนักโมเลกุลเฉลี่ยเชิงจำนวน (number-average molecular weight) ของยางทั้งสองชนิดลดลงประมาณครึ่งหนึ่ง เมื่อปฏิกิริยาดำเนินไป 2-3 ชั่วโมง และการกระจายของน้ำหนักโมเลกุลเกือบไม่เปลี่ยนแปลงระหว่างที่เกิดปฏิกิริยา