

# ADVANTAGE OF 1,2-POLYBUTADIENE ON CSM RUBBER APPLICATIONS

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Liquid polybutadiene with a higher content of 1,2-vinyl units (1,2-PB, Figure 1) can be produced by the living-anion polymerization method. It used as an additive for various rubber products such as EPDM, SBS, and HNBR, since the 1,2-vinyl units crosslink with each other to create a network formula which contributes to the improvement of hardness, elasticity and oil-resistance in the finished rubber products. In this study, we carried out the evaluation of the epoxidized 1,2-PB (1,2-Epoxidized PB) as an additive for the formulation of chlorosulfonated polyethylene (CSM) rubber. The resulting product offered excellent resistance against liquids tested in this evaluation, in addition to equivalent or superior mechanical properties such as tensile strength, hardness and compression set. The result indicates that the 1,2-Epoxidized PB can be used, not only as a modifier for mechanical properties, but also as an acid acceptor for halogenated rubber formulations instead of lead monoxide, which has seen stricter regulations by the amendment of REACH and RoHS.

Key Words: Polybutadiene, 1,2-epoxidized polybutadiene, Acid Acceptor, Chlorosulfonated polyethylene(CSM)

## INTRODUCTION

CSM contains functional groups that produce acidic substances in rubber, such as hydrogen chloride. Since these halogenated rubbers release some of the acidic substances during kneading, the addition of acid acceptors is required. Lead monoxide had been commonly used as an acid acceptor. However, it is being replaced by magnesium oxide or other acid acceptors since the use of lead compounds was regulated in Europe.

When 1,2-PB is added in rubber products as a crosslinking agent, a three-dimensional network can be formed which contributes to the improvement of hardness, elasticity, oil and water resistance. The crosslinking reaction of 1,2-vinyl units cannot be expected when using 1,4-polybutadienes (1,4-PB, Figure 2)<sup>1) 2)</sup>, which contain a much lower content of 1,2-vinyl units. In this study, we carried out the evaluation of 1,2-Epoxidized PB as an additive for the formulation of CSM rubber.

## EXPERIMENTAL DETAILS

1,2-Epoxidized PB (NISSO-PB JP-100) contains epoxy units that act as acid acceptors<sup>3) -6)</sup>. Approximately 25% of the butadiene units in the molecular chain are epoxidized. 1,2-Epoxidized PB has been commonly used as a modifier to enhance the tenacity of the epoxy curing system for adhesives, paints, and coatings. The structural difference of 1,2-Epoxidized PB and epoxidized 1,4-PB (1,4-Epoxidized PB) are shown in Figure 3.

The main materials used for this evaluation were; CSM (TS-530, Tosoh Corporation), fatty acid ester (SPLENDER R-300V, Kao Corporation), FEF carbon black (SEAST SO, Tokai Carbon Co., Ltd.), di(2-ethylhexyl)azelaate (DOZ, Taoka Chemical Co., Ltd.), dicumyl peroxide (PERCUMYL D, NOF Corporation), triallyl isocyanurate (TAIC, Mitsubishi Chemical Corporation) and 1,2-Epoxidized PB (NISSO-PB JP-100, Nippon Soda Co., Ltd.). The reference acid acceptors used were lead monoxide

(LANXESS, RHENOGRAN PbO-80), magnesium oxide (#150, Kyowa Chemical Industry Co., Ltd.), hydrotalcite (DHT 4A-2, Kyowa Chemical Industry Co., Ltd.) and 1,4-Epoxidized PB (prepared in house for this study).

The compound of CSM (100 phr), fatty acid ester (3 phr), FEF carbon black (30 phr), DOZ (10 phr), triallyl isocyanurate (4 phr) and acid acceptor (10 phr - 25 phr) were kneaded by Banbury mixer (Toyo Seiki, Labo Plastomill BR600) at 30 rpm - 50 rpm, at  $50\pm 1$  °C. The kneaded compound and dicumyl peroxide (3 phr) were mixed and milled in a two-roll rubber mill (Ikeda Kikai Kogyo Co., Ltd.) at 20 rpm, at 23 °C. CSM rubber was prepared by using an electric heat press (Ohtake Machinery) at 160 °C for 15 min - 30 min, and test pieces were obtained by cutting into JIS dumbbell No.3 test piece size. The amount of acid acceptor was adjusted so that the hardness of the rubber was equal to the resulting hardness when lead monoxide was used. The concentration of 1,2-Epoxidized PB was varied for additional evaluations.

All evaluations were performed according to ISO standards. Mooney viscosity and hardness were measured by ASKER Durometer Type A (Koubunshi Keiki Co., Ltd.) according to ISO 289-2 and ISO 7619-1 respectively. Tensile strength was measured by SHIMADZU Autograph AG-IS according to ISO 37 (sample size: 2 mmT x 5 mmW x 20 mmL, test speed: 500 mm/min, temperature:  $23\pm 1$  °C). Tearing test was carried out by SHIMADZU Autograph EZ-LX according to ISO 34-1 (sample size: 2 mmT x 5 mmW x 200 mmL, test load: 1 kN, test speed: 500 mm/min). Compression set was measured by UESHIMA Geer Aging Oven AG-1110 according to ISO 815-1 and ISO 815-2 (compression ratio: 25%, compression time: 72 hours, temperature:  $100\pm 1$  °C). Liquid resistance, by volumetric change ratio, and hardness change in test samples were evaluated by Toyo Seiki Test Tube Aging Tester Densimeter H according to ISO 1817. Samples (2 mmT x 25 mmW x 25 mmL) were immersed in 1) D.I. water, 2) chlorine aqueous solution (600 ppm), 3) HCl aqueous solution (20 wt%) and 4) HNO<sub>3</sub>

aqueous solution (10 wt%) at  $80\pm 2$  °C for 168 hours. The volumetric change ratio (%) and hardness change were compared.

## RESULTS AND DISCUSSION

The comparison of physical properties is shown in Table 1. In each case 1,2-Epoxidized PB was used, much lower Mooney viscosity ML (1+4) was obtained. In the case 10 phr of 1,2-Epoxidized PB was added, tensile strength was equivalent to the cases where the reference acid acceptors were used, while hardness was increased as the amount of 1,2-Epoxidized PB was increased. In all cases where 1,2-Epoxidized PB was added, elongation at break was equivalent to the case of using lead monoxide, while it was lower than the cases where magnesium oxide or hydrotalcite was used. In the case where 10 phr of 1,2-Epoxidized PB was added, 100% modulus was lower than lead monoxide and equivalent to magnesium oxide or hydrotalcite. However, it was increased as the amount of 1,2-Epoxidized PB was increased. For all cases where 1,2-Epoxidized PB was added, tear strength was higher than lead monoxide and hydrotalcite, or equivalent to Magnesium Oxide. In the case where 10 phr of 1,2-Epoxidized PB was added, compression set was higher than the cases where the other acid acceptors were used. However, it was reduced as the amount of 1,2-Epoxidized PB was increased. It is considered that these changes of physical properties were brought on by the network formula from the crosslinking reaction of the remaining 1,2-vinyl units in 1,2-Epoxidized PB and thus the network formula was strengthened as the amount of 1,2-Epoxidized PB was increased.

The comparison of liquid resistance is shown in Figure 4 and Figure 5. In the case 1,2-Epoxidized PB was used, volume expansion after immersion in any of the tested liquids was as low as, or lower than the case lead monoxide was used. On the other hand, the expansion ratio was much higher in the cases where magnesium oxide or hydrotalcite were used (Figure 4). Also, it was found that hardness deterioration after immersion in any

of the tested liquids could be minimized when 1,2-Epoxydized PB was used (Figure 5).

Magnesium oxide and hydrotalcite accept the chlorine ions released during the preparation of CSM rubber. As a result, magnesium chloride and aluminum chloride are generated respectively. These salts are highly soluble in water. Lead monoxide accepts chlorine ions to become lead chloride which exhibits low water-solubility (1g/100g H<sub>2</sub>O). This is suggesting that the liquid resistance is subject to the water-solubility of these chloride salts. In other words, when CSM rubber containing magnesium oxide or hydrotalcite comes into contact with a water or acid solution, it has to swell due to the generation of salts with high water-solubility. On the other hand, CSM rubber containing 1,2-Epoxydized-PB does not swell, owing to its low water-solubility (<1g/100g H<sub>2</sub>O).

The comparison of the nitric acid resistance of 1,2-Epoxydized PB and 1,4-Epoxydized PB is shown in Table 2. In the case 1,2-Epoxydized PB was used, both volume and hardness were much more stable compared with the case where 1,4-Epoxydized PB was used. This result indicates the liquid resistance depends on the epoxy units of polybutadiene.

The structures of 1,2-Epoxydized PB and 1,4-Epoxydized PB are as shown in Figure 3. The structural differences are; 1) the distance of the epoxydized unit from the main chain in 1,2-Epoxydized PB is one carbon longer than the one in 1,4-Epoxydized PB, 2) the epoxydized unit of the 1,2-Epoxydized PB can rotate. The epoxydized unit of 1,2-Epoxydized PB is less subject to steric hinderance compared with the one of 1,4-Epoxydized PB. Therefore, 1,2-Epoxydized PB has an advantage in terms of the ring-opening reactivity of epoxydized units, and works as a more efficient acid acceptor compared with 1,4-Epoxydized PB.

## CONCLUSIONS

The results of this study showed various advantages of 1,2-Epoxydized PB for CSM rubber applications. Physical properties such as Mooney viscosity, hardness, tensile

strength, tear strength and compression set could be improved by using 1,2-Epoxydized PB for CSM rubber, owing to the crosslinking reaction of the 1,2-vinyl units. In addition, CSM rubber using 1,2-Epoxydized PB showed equivalent or superior liquid resistance compared with the reference acid acceptors or 1,4-Epoxydized PB.

Lead monoxide, which had been commonly used as an acid acceptor, is being replaced by magnesium oxide or other acid acceptors since the use of lead compounds was regulated in Europe. This study demonstrated that 1,2-Epoxydized PB can add better mechanical properties and liquid resistance to CSM rubber compared with the acid acceptors commonly being used to replace lead monoxide.

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## 1,2-Polybutadiene is manufactured and sold by NIPPON SODA CO.,LTD.



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Table 1. Comparison of Physical Properties

		A	B	C	D	E	F
Mooney viscosity	ML (1+4) 100 °C	50	38	44	22	18	16
Mooney Scorch	125 °C/5 min	41.5	25.9	12.8	8.3	8.4	7.6
	125 °C/35 min	>60	>60	28.2	14.1	13.4	12
Hardness (JIS A)		59	59	62	62	70	75
Tensile Strength	MPa	19.2	13.6	19.6	19.4	19.3	19.8
Elongation at Break	%	370	380	200	200	220	180
100% Modulus	MPa	2.8	2.9	5.2	3.4	7.4	11
Tear Strength (JIS B)	N/mm	40.4	34.3	33	45	43	39.1
Compression Set	%	26	19	19	33	18	18

A: Magnesium Oxide

B: Hydrotalcite

C: Lead Monoxide

D: 1,2-Epoxidized PB (10 phr)

E: 1,2-Epoxidized PB (15 phr)

F: 1,2-Epoxidized PB (20 phr)

Table 2. Comparison of The Nitric Acid Resistance

	1,2-Expoxidized PB (15 phr)	1,4-Expoxidized PB (15 phr)
Volume Expansion Ratio (%)	2	39
Hardness Change	0	-14

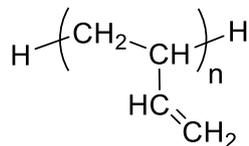


Figure 1. Structure of 1,2-PB

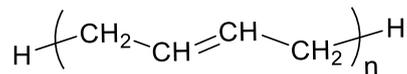
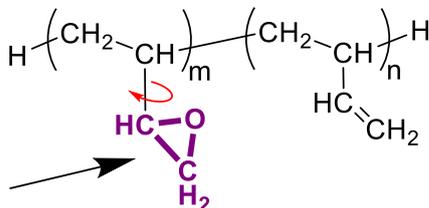
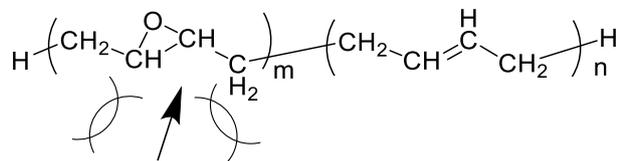


Figure 2. Structure of 1,4-PB



1,2-Epoxidized PB



1,4-Epoxidized PB

Figure 3. Structural Difference of 1,2-Epoxidized PB and 1,4-Epoxidized PB

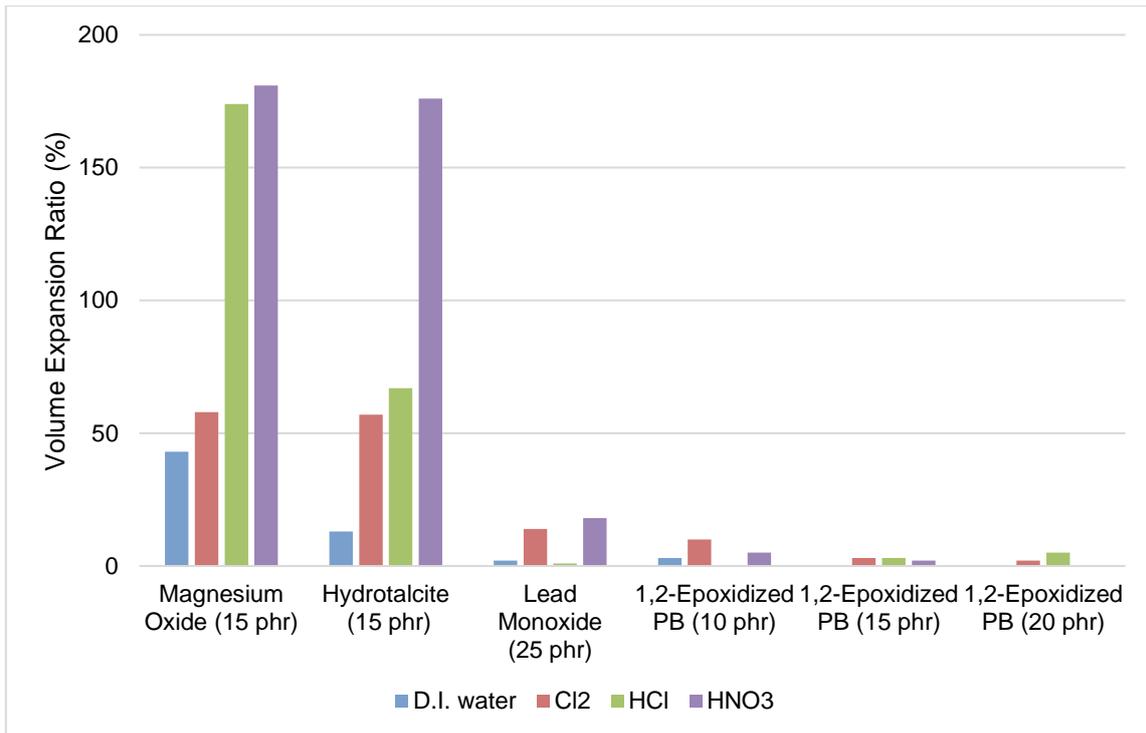


Figure 4. Comparison of Volumetric Expansion Ratio

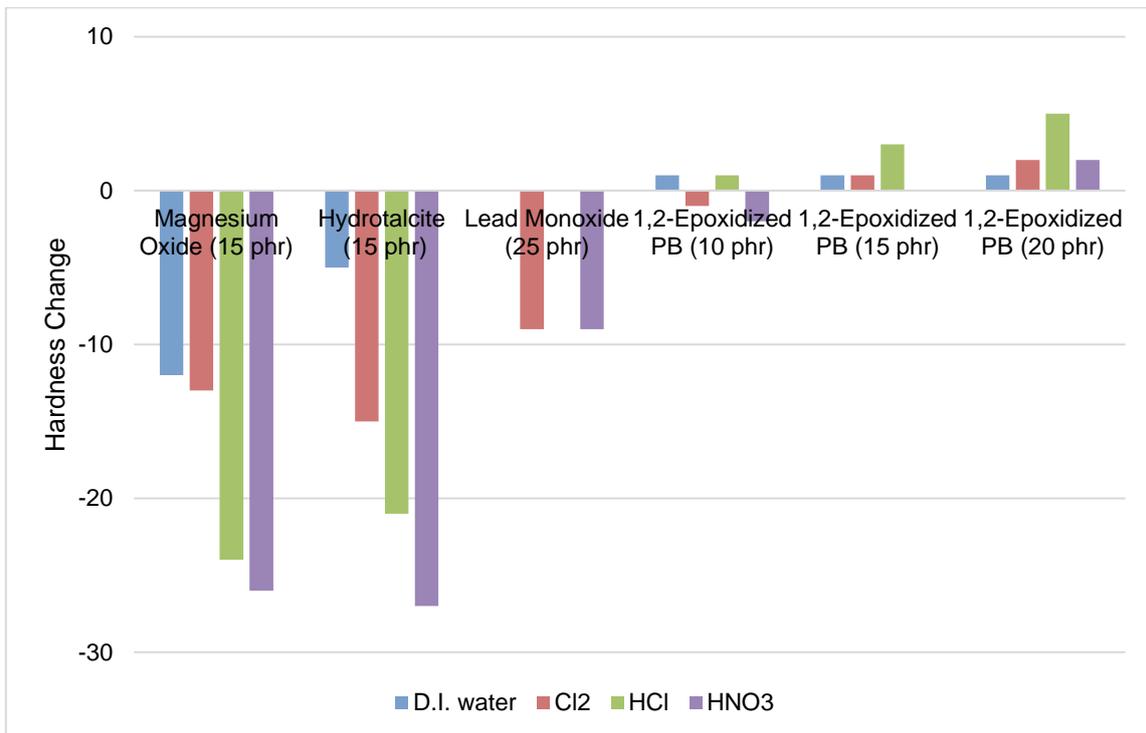


Figure 5. Comparison of Hardness Change

