

Oxidation Behavior of Isoprene/Styrene Copolymer and Butadiene/Styrene Copolymer

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Synopsis

The oxidation behavior of emulsion isoprene/styrene copolymer (SIR) and emulsion butadiene/styrene copolymer (SBR) by heat aging or ultraviolet irradiation in air has been investigated from the change of gel fraction, intrinsic viscosity, molecular weight distribution, and mechanical properties. Upon oxidation by heat aging, SIR predominantly undergoes chain scission and shows only a slight change of mechanical properties, whereas SBR predominantly undergoes crosslinking and sharply becomes brittle. Upon oxidation by ultraviolet irradiation, SIR undergoes both chain scission and crosslinking and shows almost no substantial change in mechanical properties, whereas SBR predominantly undergoes crosslinking and sharply becomes brittle. The probability ratio of chain scission to crosslinking with oxidation by heat aging or ultraviolet irradiation was determined by the method of Charlesby et al. The results can reasonably explain the oxidation behavior of the copolymers described above.

INTRODUCTION

The oxidation of diene polymers has so far been investigated intensively by a number of workers.^{1,2} Cole et al.³ have demonstrated that, when heated at 125°C in the presence of oxygen, isoprene polymers such as natural rubber, emulsion polyisoprene, and emulsion isoprene/styrene copolymer (SIR) undergo chain scission, whereas butadiene polymers such as emulsion polybutadiene and emulsion butadiene/styrene copolymer (SBR) undergo crosslinking, and the difference in the oxidation behavior can qualitatively be explained by the difference in chemical reactivity of isoprene polymers and butadiene polymers.

It seems to be of great use from the practical point of view to clarify the difference in the oxidation behavior of isoprene polymers and butadiene polymers more precisely. In the above-mentioned investigation of Cole et al., polymers containing antioxidant which may affect the oxidation behavior of polymers were used. Consequently, in the present paper the oxidation of SIR and SBR by heat aging or ultraviolet irradiation will be dealt with to elucidate the difference in the oxidation behavior of isoprene polymers and butadiene polymers.

EXPERIMENTAL

Preparation and Purification of the Copolymers

SIR was prepared and purified by the following procedures. Polymerization was carried out at 5°C by the usual method of emulsion polymerization according

TABLE I
Polymerization Recipe for Preparation of SIR

Ingredient	Amount, weight parts
Water	200
Isoprene	65
Styrene	35
Sodium dodecylbenzene sulfonate	6.72
Cumene hydroperoxide	0.63
Iron(II) sulfate-water (1/7)	1.00
Sodium pyrophosphate	0.96
<i>tert</i> -Dodecyl mercaptan	0.086

to the polymerization recipe in Table I, where ingredients were purified, if necessary, by the usual method. At a conversion of 65%, the latex was poured into a large amount of isopropyl alcohol. The coagulated copolymer was washed vigorously with water and methyl alcohol and dried *in vacuo* at room temperature.

Cold SBR (Krylene 1515) obtained from Polymer Corp. Ltd. was purified twice by dissolving in toluene and reprecipitating with methyl alcohol and dried *in vacuo* at room temperature. The removal of antioxidant by the purification was confirmed by observing the ultraviolet spectrum of the copolymer in tetrahydrofuran solution at 275–300 $m\mu$, which is the characteristic absorption band of antioxidant.

Characterization of the Copolymers

The composition of copolymer was determined by NMR measurement.

The gel fraction of copolymer was determined from the sol fraction measured by the following procedure. After the copolymer was immersed in toluene at 30°C for 20 hr, gel was removed by centrifugation and filtration. Then, the amount of sol in the filtrate was measured gravimetrically.

After removing gel by the above-described method, the intrinsic viscosity of the copolymer was measured in toluene solution at 30°C with an Ubbelohde viscometer.

The gel permeation chromatography (GPC) of copolymer was measured, after removing gel by the above-described method, in tetrahydrofuran solution at 35°C. The molecular weight distribution of copolymer was determined by analyzing the result of GPC on the assumption that the fractionation in GPC is governed substantially by the chain length. In this case, the microstructure of copolymer^{4,5} as well as the composition of copolymer were taken into account.

TABLE II
Characterization Results of the Copolymers

Copolymer	Composition, wt-%			Gel fraction, wt-%	Molecular weight	
	Isoprene	Butadiene	Styrene		Weight-average	Number-average
SIR	74	—	26	0.0	2.27×10^5	4.53×10^4
SBR	—	72	28	0.0	1.69×10^5	4.82×10^4

The stress-strain curve of copolymer was measured on the 2-cm-long, 0.5-cm-wide, and 0.05-cm-thick sample at 25°C with the deformation rate of 0.5 cm/min. The Young's modulus was determined from the initial slope of the stress-strain curve.

The characterization results of the copolymers described above are shown in Table II. It is apparent from Table II that both copolymers have almost the same styrene fraction and molecular weight, which indicates that these copolymers are appropriate samples for the investigation of oxidation behavior.

Oxidation of the Copolymers

The oxidation of the copolymers in Table II was performed in air on films 0.05 cm thick.

The oxidation by heat aging was carried out at 70°C in a Shimadzu YSL-1S electric oven.

The oxidation by ultraviolet irradiation was carried out at 40°C with a carbon-arc lamp in a Shimadzu CF-20S Fade-meter.

RESULTS AND DISCUSSION

Heat Aging of the Copolymers

The change of the gel fraction and intrinsic viscosity of the copolymers with oxidation by heat aging is shown in Table III. It is apparent from Table III that SIR exhibits a slight increase in gel fraction and a sharp decrease in intrinsic viscosity, whereas SBR exhibits a sharp increase in gel fraction and a gradual decrease in intrinsic viscosity. This indicates that SIR predominantly undergoes chain scission, whereas SBR predominantly undergoes crosslinking, which is approximately consistent with the oxidation behavior of isoprene polymers and butadiene polymers reported by Cole et al.³ It seems from Table III that SBR

TABLE III
Change in Gel Fraction and Intrinsic Viscosity of the Copolymers with Oxidation by Heat Aging

Copolymer	Aging time, hr	Gel fraction, wt-%	Intrinsic viscosity, dl/g
SIR	0	0.0	1.46
	6	0.0	0.98
	12	0.0	0.75
	24	trace	0.79
	36	trace	0.64
	48	2.3	0.70
	72	3.9	0.71
	96	6.7	0.68
	144	5.7	0.69
	SBR	0	0.0
24		trace	2.00
36		trace	2.04
48		0.7	1.93
72		23.6	1.45
96		39.1	1.02
144		81.3	1.21

TABLE IV
Change in Mechanical Properties of the Copolymers with Oxidation by Heat Aging

Copolymer	Aging time, hr	Young's modulus, kg/cm ²	Tensile strength, kg/cm ²	Elongation at break, %
SIR	0	4.6	0.4 ^a	1000 ^b
	6	1.3	0.2 ^a	1000 ^b
	12	0.9	0.1 ^a	1000 ^b
	24	1.7	0.2 ^a	1000 ^b
	48	1.0	0.2 ^a	1000 ^b
	96	2.5	0.2	680
	144	2.5	0.4	360
SBR	0	7.2	1.0	450
	24	4.6	0.9	810
	36	4.5	0.9	780
	48	4.6	1.2	930
	72	7.2	2.3	730
	96	14.7	3.0	175
	96	14.7	3.0	175
	144	26.5	5.9	35

^a The stress observed at elongation of 1000%.

^b Larger than 1000%.

does not exhibit any remarkable change with oxidation in the initial 24 hr. This may be attributed to a trace amount of antioxidant remaining without being removed by the purification and may not represent typical oxidation behavior of SBR. Detailed discussion of this problem will be given elsewhere.

The changes in mechanical properties and the stress-strain curves of the copolymers with oxidation by heat aging are shown in Table IV and Figure 1, respectively. It is apparent from Table IV and Figure 1 that SIR exhibits a gradual decrease in Young's modulus and tensile strength in the initial 48 hr, then a gradual increase in Young's modulus and tensile strength, and a gradual decrease

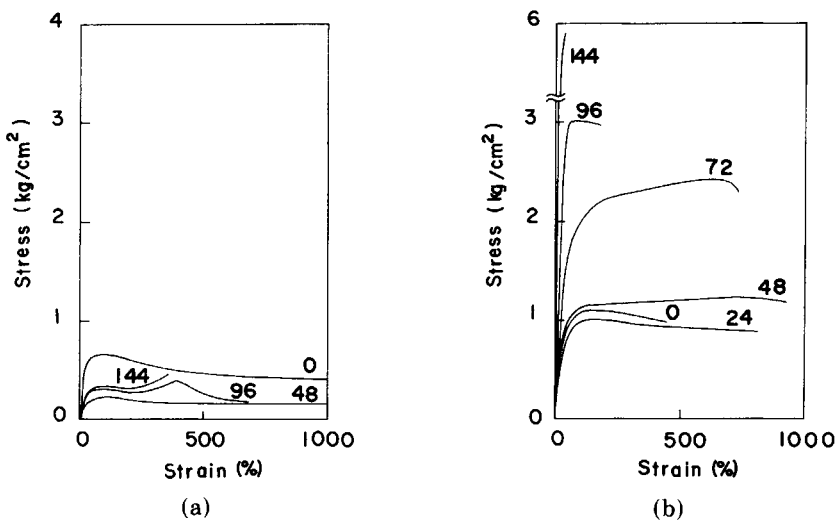


Fig. 1. Change in stress-strain curve of copolymers with oxidation by heat aging: (a) SIR; (b) SBR. Figures on curves indicate aging time in hours.

TABLE V
Change in Gel Fraction and Intrinsic Viscosity of the Copolymers with
Oxidation by Ultraviolet Irradiation

Copolymer	Irradiation time, hr	Molecular weight		
		Weight-average	Number-average	
SIR	0	2.27×10^5	4.53×10^4	
	1	2.40×10^4	3.86×10^3	
	2	3.84×10^4	3.91×10^3	
	5	1.69×10^5	4.82×10^4	
	10	2.74×10^4	5.11×10^3	
	20			
	50			
	100			
	SBR	0		
		1		
2				
5				
10				
20				
50				
75				
100				
200				

in elongation at break in the next 96 hr. On the other hand, SBR exhibits a sharp increase in Young's modulus and tensile strength and a sharp decrease in elongation at break. This is closely correlated with the change of the gel fraction and intrinsic viscosity of the copolymers in Table III, as is expected from the theory.⁶

Ultraviolet Irradiation of the Copolymers

The change in gel fraction and intrinsic viscosity of the copolymers with oxidation by ultraviolet irradiation is shown in Table V. It is apparent from Table V that SIR exhibits a slight increase in gel fraction and a sharp decrease in intrinsic viscosity in the initial 20 hr, then a sharp increase in gel fraction and a gradual decrease in intrinsic viscosity in the next 80 hr. SBR, on the contrary, exhibits a sharp increase in gel fraction and a sharp decrease in intrinsic viscosity. This indicates that SIR undergoes both chain scission and crosslinking with

TABLE VI
Change in Molecular Weight of the Copolymers with Oxidation by
Ultraviolet Irradiation

Copolymer	Irradiation time, hr	Molecular weight	
		Weight-average	Number-average
SIR	0 ^a	2.27×10^5	4.53×10^4
	2	2.40×10^4	3.86×10^3
	100	3.84×10^4	3.91×10^3
SBR	0 ^a	1.69×10^5	4.82×10^4
	75	2.74×10^4	5.11×10^3

^a See also Table II.

TABLE VII
Change in Mechanical Properties of the Copolymers with Oxidation by
Ultraviolet Irradiation

Copolymer	Irradiation time, hr	Young's modulus, kg/cm ²	Tensile strength, kg/cm ²	Elongation at break, %
SIR	0	3.7	0.4 ^a	1000 ^b
	1	2.6	0.3 ^a	1000 ^b
	5	2.7	0.4 ^a	1000 ^b
	10	5.8	0.4	805
	20	5.0	0.5 ^a	1000 ^b
	50	4.5	0.7 ^a	1000 ^b
	100	—	1.5 ^a	1000 ^b
SBR	0	5.5	1.0	450
	1	5.9	2.0 ^a	1000 ^b
	2	7.4	4.1 ^a	1000 ^b
	5	8.7	4.1	410
	10	10.4	4.1	205
	20	34.2	3.9	230
	50	46.8	4.7	250
	100	110.0	5.5	200
	200	128.0	7.1	50

^a The stress observed at elongation of 1000%.

^b Larger than 1000%.

oxidation by ultraviolet irradiation, whereas SBR predominantly undergoes crosslinking. This behavior is somewhat similar to that in the oxidation by heat aging. It seems, however, that the substantial increase in gel fraction of SIR after irradiation of fairly long duration is characteristic of oxidation by ultraviolet irradiation.

The changes in molecular weight distribution and molecular weight of the copolymers with oxidation by ultraviolet irradiation are shown in Figure 2 and Table VI, respectively. It is apparent that SIR shows a remarkable decrease

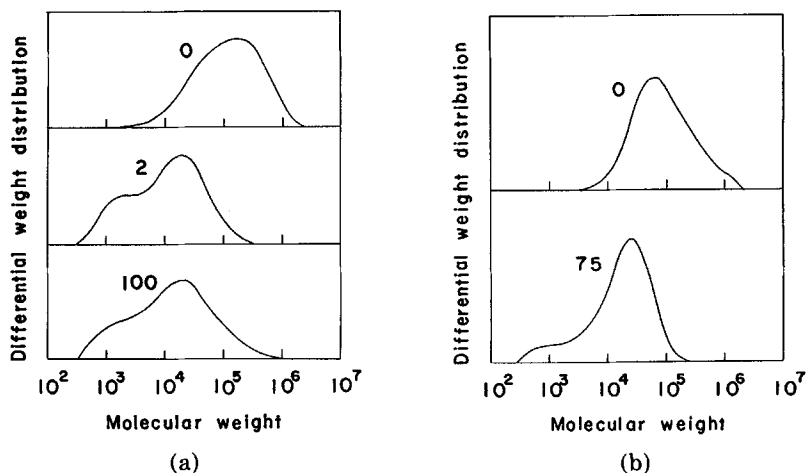


Fig. 2. Change in molecular weight distribution of copolymers with oxidation by ultraviolet irradiation: (a) SIR; (b) SBR. Figures on curves indicate irradiation time in hours.

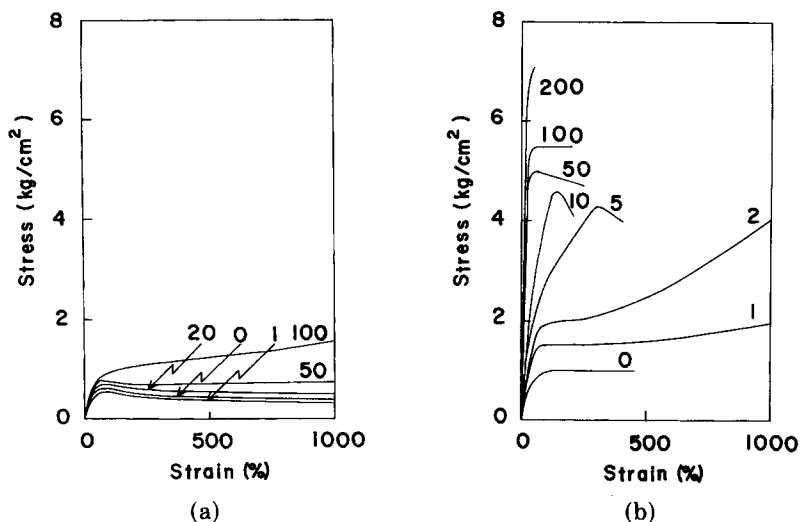


Fig. 3. Change in stress-strain curve of copolymers with oxidation by ultraviolet irradiation: (a) SIR; (b) SBR. Figures on curves indicate irradiation time in hours.

in molecular weight and an increase in an extremely low molecular weight fraction which cannot appreciably be found in the original copolymer with irradiation of 2 hr and a slight increase in high molecular weight fraction with irradiation of 100 hr. This can reasonably be explained by the above-described oxidation behavior of SIR, that is, chain scission and successive substantial crosslinking.

It is apparent from Figure 2 and Table VI that SBR also shows a remarkable decrease in molecular weight and an increase in an extremely low molecular weight fraction which cannot appreciably be found in the original copolymer with irradiation of 75 hr. This indicates that in this case, although crosslinking with which the high molecular weight fraction may selectively form gel predominates, chain scission also occurs to some extent.

In Table VII and Figure 3 are shown the change in mechanical properties and stress-strain curve of the copolymers with oxidation by ultraviolet irradiation, respectively. It is apparent that SIR exhibits only a slight increase in Young's modulus and tensile strength, whereas SBR exhibits a sharp increase in Young's modulus and tensile strength and a sharp decrease in elongation at break. This is almost consistent with the change in gel fraction and intrinsic viscosity of the copolymers in Table V, as can be expected from the theory.⁶

Oxidation Behavior of the Copolymers

It is apparent from the above-described considerations that SIR and SBR undergo both chain scission and crosslinking with oxidation by heat aging or ultraviolet irradiation. In this case, the probability ratio of chain scission to crosslinking can be determined by the theory of Charlesby et al.⁷ Although this theory was originally derived for high-energy irradiation, it is applicable also to heat aging⁸ or ultraviolet irradiation.⁹

In applying this theory to heat aging or ultraviolet irradiation, the radiation dose may be replaced by the time of heat aging or ultraviolet irradiation. Then,

TABLE VIII
Oxidation Behavior of Copolymers

Copolymer	Probability ratio of chain scission to crosslinking ^a	
	Heat aging	Ultraviolet irradiation
SIR	1.9	1.1
SBR	0.2	0.2

^a p_0/q_0 in eq. (1).

the relationship between sol fraction s and the time of heat aging or ultraviolet irradiation t can be represented by the following equation:

$$s + s^{1/2} = p_0/q_0 + 1/(q_0u_1t) \quad (1)$$

where p_0 and q_0 are extents of chain scission and crosslinking, respectively, per unit time of heat aging or ultraviolet irradiation, and u_1 is the number-average molecular weight. It has been demonstrated^{8,10,11} that at a sufficiently long period of heat aging or ultraviolet irradiation, the plot of $s + s^{1/2}$ against $1/t$ becomes linear, with an intercept equal to p_0/q_0 , irrespective of the molecular weight distribution of the initial polymer. Consequently, the oxidation behavior of SIR and SBR can be represented by the probability ratio of chain scission to crosslinking, p_0/q_0 following the above-described procedure.

In Figure 4 is shown a typical relationship between $s + s^{1/2}$ and the reciprocal time of heat aging. The points in Figure 4 do not strictly fit the straight line which is expected from the theory. The discrepancy may indicate that the theory does not hold well in the case of the copolymers or that there are fairly large errors in the measurement of the gel fraction. Further investigation seems to be necessary to settle this difficulty. However, the approximate value of the probability ratio of chain scission to crosslinking p_0/q_0 may be obtained as an intercept assuming that the points approximately fit a straight line. The results of the probability ratio of chain scission to crosslinking, p_0/q_0 thus obtained are shown in Table VIII. It is apparent from Table VIII that SIR predominantly undergoes chain scission with oxidation by heat aging and undergoes both chain scission and crosslinking with oxidation by ultraviolet irradiation, whereas SBR predominantly undergoes crosslinking with oxidation both by heat aging and by

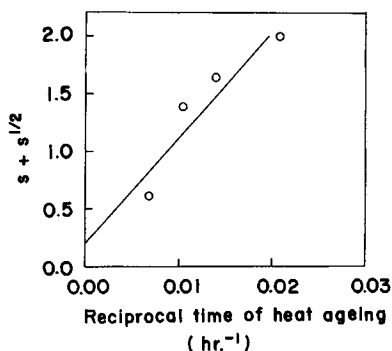


Fig. 4. Relationship between $s + s^{1/2}$ and reciprocal time of heat aging for SBR.

ultraviolet irradiation. This is consistent with the qualitative interpretation described above.

Further discussion on the relationship between the difference in the oxidation behavior of SIR and SBR and the difference in chemical reactivity of isoprene polymers and butadiene polymers will be given elsewhere.

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