

Epoxidation of Styrene-Butadiene Block Polymers. I

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Synopsis

A styrene-butadiene-styrene (20-60-20) linear block polymer was epoxidized in toluene and cyclohexane solutions with peroxyformic acid generated *in situ*. The epoxidized polymer, containing about 8% oxygen, exhibits greatly improved resistance to ASTM oils. It can be readily compounded with carbon black, and the unvulcanized stock is found to be comparable to vulcanized polychloroprene and nitrile rubber in tensile strength and resistance to ASTM oils and certain chemicals.

INTRODUCTION

Styrene-butadiene block polymers constitute an important class of thermoplastic elastomers. They behave as vulcanized rubbers at room temperature and yet can be processed as thermoplastics at elevated temperatures. As a result, they have gained considerable attention in recent years. However, their resistance to hydrocarbon oils and solvents is rather poor. Polymers with polar groups are superior in this respect, but the anionic polymerization technique employed to synthesize these block polymers is not too conducive to incorporation of polar monomers during polymerization. Under the circumstances, chemical modification to generate polar groups on the polymer appears to be a viable approach. Epoxidation is a convenient method to incorporate oxygen in the diene blocks. Work along these lines has been reported,¹ but it is restricted to liquid polybutadienes^{2,3} and styrene-butadiene block copolymers that need vulcanization.^{4,5} A patent issued to Shell⁶ describes an epoxidized styrene-butadiene block polymer in which at least 50% of the unsaturation is eliminated and the epoxide groups are hydrolyzed to make the polymer swell in water or other hydrogen-bonding solvents. It is not known whether a chemical modification of the diene block, such as by epoxidation, interferes with the domain morphology to adversely affect the physical and mechanical properties of the block polymers. The extent of modification that is necessary to bring about the resistance to hydrocarbon oils and solvents is also not known. The present investigations were carried out to answer these questions.

EXPERIMENTAL

Preparation of Styrene-Butadiene-Styrene Linear Block Polymer

Materials. Marlex-grade cyclohexane was dried by passing it through a column packed with Berl saddles while maintaining a countercurrent flow of prepurified nitrogen. Polymerization-grade butadiene was dried by distillation through a column packed with Alcoa F-1 activated alumina and stored at -16°C without inhibitor until use. Styrene was distilled, and the center cut was stored at -16°C until needed. *sec*-Butyllithium from Foote Minerals was diluted with cyclohexane to about $0.5M$ and used.

Polymerization. Polymerizations were conducted in 26-oz. beverage bottles⁷ capped with crown caps over self-sealing liners. Cyclohexane, styrene, and *sec*-butyllithium were charged in that order and tumbled in a water bath at 70°C for 30 min. Butadiene was then added and tumbling at 70°C was continued for 45 min. At this stage, styrene was again added and the bottles tumbled at 70°C for 30 min more. Polymerization was then terminated by the addition of 1 phr 2,6-di-*tert*-butyl-4-methylphenol as a 10% solution in a 1:1 mixture of toluene and isopropyl alcohol. Polymer was recovered by coagulation in isopropyl alcohol and dried in a vacuum oven overnight at 60°C. Polymer so prepared is described in Table I.

Epoxidation of Styrene-Butadiene Block Polymer

Materials. Formic acid (88%) and hydrogen peroxide (30%) used in this work were obtained from J. T. Baker Co. Toluene and isopropyl alcohol were procured from Malinckrodt Chemicals.

Procedure. In a typical epoxidation run, 40 g polymer was dissolved in 400 ml toluene (or cyclohexane, where mentioned) in a 1-liter three-necked glass flask equipped with a mechanical stirrer, a thermometer, and an addition funnel. The polymer solution was heated to, and maintained at, the desired temperature with the aid of a hot-water bath. Required volume of formic acid was added, followed by a dropwise addition of a measured volume of 30% hydrogen peroxide. The reaction mixture was stirred for a predetermined time. After completion of the reaction, the polymer was coagulated in isopropyl alcohol and was purified by re-coagulating two more times in isopropyl alcohol from toluene solutions. One phr 2,6-di-*tert*-butyl-4-methylphenol was added to the polymer solution prior to last coagulation. The coagulated polymer was then dried at 60°C under vacuum.

Analysis of Products. Epoxidized polymers were analyzed for their oxirane contents by the method described by Jay.⁸ Total oxygen contents were determined by neutron activation analysis.

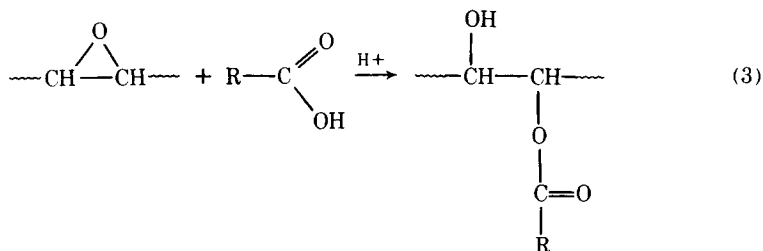
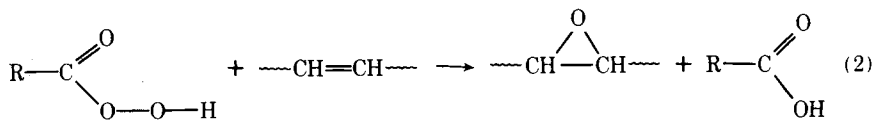
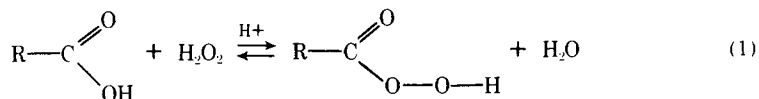
RESULTS AND DISCUSSION

Unsaturated polymers can be epoxidized either by preformed peroxy acids or by *in situ* methods using hydrogen peroxide and lower aliphatic acids. More efficient conversion of double bonds to oxirane groups with fewer unwanted side reactions is accomplished by using preformed peroxy acids. Since the goal of the current investigation is to incorporate polar groups, not necessarily in the

TABLE I
Styrene-Butadiene-Styrene Linear Block Polymer

S-B-S	20-60-20
\bar{M}_w/\bar{M}_n	76,000/63,000
Inherent viscosity	0.72
Styrene, %	41.1
Block styrene, %	39.4
Unsaturation, %	
Trans	31.2
Vinyl	7.1

form of oxirane groups alone, it was decided to adopt the *in situ* method. The chemistry of *in situ* epoxidation can be explained by the following scheme⁹:



It is seen from the above that the actual epoxidation takes place in step (2) and requires no catalyst. Steps (1) and (3) are acid catalyzed. Formation of peroxyacetic acid is greatly dependent upon the acid catalyst and also the concentration of hydrogen peroxide.¹⁰ In the absence of strong acid catalysts such as sulfuric acid or the ion-exchange resins of the sulfonic acid type, establishment of equilibrium in reaction (1) is impractically slow. Furthermore, in the absence of an acid catalyst, an equimolar mixture of 98% hydrogen peroxide and acetic acid produces a 50% solution of peroxyacetic acid in acetic acid at equilibrium, whereas a 30% hydrogen peroxide generates only a 10% solution of peroxyacetic acid.¹⁰ Peroxyformic acid, on the other hand, is formed rapidly at or below room temperature even with 30% hydrogen peroxide and requires no added acid catalyst. Hence, it was decided to use a combination of formic acid and 30% hydrogen peroxide in our work. Choice of 30% hydrogen peroxide is obvious for safety reasons. Formic acid, being a strong acid, is also known to open up the epoxy groups which will help incorporate a higher oxygen content in the polymer without additional reaction steps.

In order to study the effect of reaction variables such as temperature, time, and the ratio of formic acid to hydrogen peroxide on the oxirane and oxygen contents of the resulting polymers, experiments were carried out with the recipe shown in Table II. The hydrogen peroxide (0.5 mole/100 g polymer) used in this recipe should theoretically generate 8% oxirane oxygen, enough to impart good oil resistance as determined by initial trial runs. Results in Table II indicate that the rate of epoxidation increases with elevation in temperature and also with increasing HCOOH/H₂O₂ ratios. Thus, for example, epoxidations carried out for 3 hr at 25°C with HCOOH/H₂O₂ ratios of 0.5 and 1.5 generated polymers with 1.9% and 5.1% oxirane contents, whereas at 50°C they were 4.6% and 5.6%, respectively. As much as 5.1% oxirane content could be incorporated in the polymer within 30 min at 50°C using a HCOOH/H₂O₂ ratio of 1.5.

Generally, the rates of epoxidation seemed to increase with time for the first

TABLE II
Effect of Temperature, Time, and Stoichiometry on Epoxidation of Styrene-Butadiene Linear Block Polymer

Formic acid		Moles HCOOH/H ₂ O ₂	Temperature, °C	Time, min	Oxirane, %	Oxygen, %
Parts	Mole					
13.0	0.25	0.5	25	30	0.8	2.5
				60	1.1	2.8
				120	1.3	3.0
				180	1.9	3.7
				300	2.3	4.2
26.0	0.5	1.0	25	30	1.2	2.9
				70	1.9	3.6
				120	3.3	5.2
				180	3.8	6.6
				300	4.4	6.9
39.0	0.75	1.5	25	30	2.4	5.2
				60	3.2	5.6
				120	4.6	7.3
				180	5.1	8.0
				300	5.5	8.2

Parts

Polymer
Toluene
88% Formic acid
30% Hydrogen peroxide
Temperature
Time

100
860
variable
56 (0.5 mole)
variable
variable

13.0	0.25	0.5	50	30	2.6	4.9
				60	3.2	5.6
				140	4.1	6.4
				180	4.6	8.0
				300	4.4	9.5
26.0	0.5	1.0	50	30	3.9	6.2
				60	4.8	7.6
				120	5.4	8.3
				220	5.7	9.5
				300	5.6	9.5
39.0	0.75	1.5	50	30	5.1	9.5
				60	5.6	10.4
				120	5.8	10.4
				180	5.6	9.5
				300	5.4	11.28

3 hr leading to a plateau effect. Samples withdrawn later at 50°C exhibited a gradual decrease in their oxirane contents, and such a tendency seemed to increase with increasing HCOOH/H₂O₂ ratios. The drop in oxirane content was invariably accompanied by an increase in the total oxygen content, which seems to corroborate an earlier statement about the opening of the epoxide rings to form hydroxy and formate ester groups. It is also noticed that about 8% total oxygen in the polymer can be incorporated both at 25°C (HCOOH/H₂O = 1.5) and at 50°C. For that matter, the ratio of formic acid to hydrogen peroxide does not seem to be very critical at 50°C, particularly when the epoxidation reaction is carried out for 3 hr or longer.

A polymer sample was then epoxidized and evaluated, with results shown in Table III. Although there was not much of a change in the tensile property of the epoxidized polymer over that of the parent, the epoxidized polymer was more rubbery, with a lower set at break, lower shore hardness, and higher melt flow. There was also a considerable improvement in the resistance to ASTM oils # 1, # 2, and # 3 and ASTM fuel A after epoxidation. The epoxidized polymer exhibited a tensile strength of 11 MPa after immersion in ASTM oil # 3 for seven days at room temperature, whereas the parent polymer dissolved under these conditions. Resistance to ASTM fuels B and C was however poor for both the epoxidized and parent polymers.

Choice of toluene as a solvent for epoxidation was arbitrary, although it was somewhat influenced by the favorable reports on aromatic solvents in the liter-

TABLE III
Epoxidation and Evaluation of Styrene-Butadiene Linear Block Polymer

	Parts	
Polymer	100	
Toluene	860	
88% Formic acid	26	
30% Hydrogen peroxide	56	
Temperature, °C	50	
Time, hr	3	
	Epoxidized polymer	Parent polymer
% Oxirane	5.5	0
% Oxygen	9.3	0
Melt flow (180°C, 5 kg)	5.6	3
	Original	
300% Modulus, MPa	3.0	5.2
Tensile strength, MPa	34.3	31.4
Elongation, %	690	730
Shore A hardness	86	92
Set at break, %	17	48
	Aged 7 Days in ASTM Oil # 3 at Room Temperature	
Tensile strength, MPa	11.0	dissolved
	% Swell After 7 Days at Room Temperature	
ASTM Oil # 1	1.6	9.3
# 2	6.8	15.9
# 3	22.8	159
Fuel A	20.8	173.8
B	dissolved	dissolved
C	dissolved	dissolved

TABLE IV
Epoxidation of Styrene-Butadiene Linear (20-60-20) Block Polymer in Cyclohexane at 70 °C

		Parts			
Polymer		100			
Cyclohexane		780			
88% Formic acid		variable			
30% Hydrogen peroxide		56			
Temperature, °C		70			
Time		variable			

Formic acid		Moles HCOOH/H ₂ O ₂	Time, min	Oxirane, %	Oxygen, %
Parts	Mole				
26.0	0.5	1.0	30	3.8	7.6
			60	4.2	8.1
			120	4.5	8.5
			180	4.4	8.7
			300	4.5	8.7
39.0	0.75	1.5	30	3.8	7.2
			60	4.2	7.9
			120	4.5	8.2
			180	4.0	8.2
			300	3.8	8.5

TABLE V
Epoxidation of Styrene-Butadiene Linear (20-60-20) Block Polymer for Evaluation in Compounded Stocks

		Parts
Polymer		100
Cyclohexane		780
88% Formic acid		26
30% Hydrogen peroxide		56
Temperature, °C		70
Time, hr		2
Oxirane content, %		4.4
Total oxygen content, %		7.6

ature.^{10,11} It would be worthwhile, however, to investigate cyclohexane as a solvent since styrene-butadiene block polymers are normally prepared in that solvent and it should help epoxidize the polymer cements directly. Initial work on epoxidation in our laboratories using cyclohexane as a solvent and the recipe given in Table II indicated that there was a tendency for the epoxidized polymer to precipitate at 50°C. Raising the temperature to 70°C, however, seemed to solve this problem.

In order to study the effect of cyclohexane on the oxirane and oxygen contents of the resulting polymers, a few experiments were conducted at 70°C as shown in Table IV. A comparison of the data in Tables IV and II (toluene) points out that incorporation of oxirane and oxygen contents in cyclohexane proceeds in a manner similar to that in toluene but that the actual oxirane and oxygen contents of the polymers epoxidized in cyclohexane are generally lower than the corresponding values in toluene. It is also observed that the onset of the plateau effect in the case of cyclohexane at 70°C appears at about 2 hr, against 3 hr at 50°C for toluene.

TABLE VI
Evaluation of Epoxidized Styrene-Butadiene (40-60) Block Polymer in Compounded Stocks

	1	2	3	4	5
Philprene 1503	100	—	—	—	—
Neoprene W ^b	—	100	—	—	—
Paracril BJ ^c	—	—	100	—	—
Epoxidized Polymer	—	—	—	100	—
Parent polymer	—	—	—	—	100
C-Black N550	40	40	40	40	40
Zinc oxide	5	5	5	5	5
Stearic acid	2	0.5	2	2	2
Santocure	0.12	—	1.5	—	—
Sulfur	—	—	—	—	—
Magnesium oxide	—	4	—	—	—
NA 22	—	0.5	—	—	—
Monex	—	—	0.5	—	—
200% Modulus, MPa	2.8	12.9	6.6	19.0	7.6
300% Modulus, MPa	5.3	21.2	12.2	—	10.7
Tensile, MPa	19.7	21.9	18.3	23.4	17.9
Elongation, %	780	310	420	240	730
Crescent tear, lb/in.	350	260	195	290	385
Gehman freeze point, °C	-55	-43	-30	-58	plastic-type curve
Shore A hardness	50	67	65	88	92
	% Swell, 7 Days, 78°F				
Vinegar	11	17	13	17	5
Methyl alcohol	1	6	16	10	2
Mineral oil	21	3	2	1	22
Brake fluid	4	15	35	28	7
ASTM oil #1	11	2	0.4	1	13
#2	20	5	1	3	23
#3	100	21	6	14	dissolved
Fuel A	75	20	7	19	144
Vegetable oil	36	8	1	5	57
Methyl ethyl ketone	110	142	220	204	dissolved
Dibutyl phthalate	67	113	165	165	dissolved

^a General purpose, emulsion SBR.

^b General purpose polychloroprene.

^c Nitrile rubber containing 29.5% acrylonitrile.

A sample of styrene-butadiene block polymer was then epoxidized in cyclohexane, as shown in Table V, and then evaluated, this time in compounded stocks, as described in Table VI. The epoxidized polymer was compounded with 40 phr carbon black and evaluated in comparison to vulcanized Philprene 1503, Neoprene W, and Paracril BJ (29.5% acrylonitrile) and to unvulcanized parent polymer as controls. From the results in Table VI it is noticed that the experimental polymer, containing 6.4% oxirane and 7.6% total oxygen, exhibited 200% modulus (19 MPa) and tensile strength (23.4 MPa) comparable to that of cured Neoprene (12.9 MPa and 21.9 MPa, respectively) but better than the rest of the polymers. The Gehman freeze point for the epoxidized polymer proved to be the lowest (-58°C) and was comparable to that of Philprene 1503 (-55°C). Insofar as the resistance to swelling (7 days at room temperature) in various chemicals and solvents is concerned, the epoxidized polymer exhibited low swelling in

vinegar, brake fluid, ASTM oils #1 and #2, methyl alcohol, and mineral oil and relatively high swelling in methyl ethyl ketone, and dibutyl phthalate. These results were, however, comparable to those of the control polymers. Resistance of the epoxidized polymer to swelling in ASTM fuel A, vegetable oil, and ASTM oil #3 was much superior to that of the parent polymer and Philprene 1503 and comparable to that of Neoprene W and Paracril BJ.

CONCLUSIONS

1. Epoxidation of styrene-butadiene linear block polymer by peroxyformic acid, generated *in situ*, offers a simple and practical route to improve their resistance to hydrocarbon oils.

2. Toluene is preferred to cyclohexane as the solvent medium because of efficient utilization of peroxyformic acid and the relative ease in subsequent handling of the polymer solution.

3. The epoxidized polymer can be readily compounded with carbon black. An unvulcanized stock of an epoxidized styrene-butadiene (40-60) linear block polymer was found to have good low temperature properties and was comparable to vulcanized Neoprene and Paracril rubbers in tensile strength and swell resistance to ASTM oils and other chemicals.

4. The fact that epoxidation does not adversely affect the physical and mechanical properties of the block polymers seems to indicate that such a chemical modification does not interfere with the domain morphology that is so important to these thermoplastic elastomers.

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