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Properties of Poly(Alkylene Oxide) Elastomers

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Synopsis

The catalyst comprised of triisobutylaluminum, zinc acetylacetonate, and water was used to prepare homopolymer of epichlorohydrin; copolymers of epichlorohydrin with propylene oxide, ethylene oxide, and allyl glycidyl ether; and terpolymers of epichlorohydrin, propylene oxide, and allyl glycidyl ether and of epichlorohydrin, ethylene oxide, and allyl glycidyl ether. The vulcanizates of these rubbers provide variations of stress–strain and dynamic properties, freeze point, hardness, and solvent resistance depending on the type and amount of comonomer. In general, these rubbers have excellent heat, ozone, and oxidation resistance as well as oil and solvent resistance.

INTRODUCTION

Keen interest in the polymerization of alkylene oxides in recent years has led to the development of some interesting elastomers based on these monomers. Poly(propylene oxide) rubber was first announced in 1963, and its preparation and properties were reported by Gruber et al.[1] The poly(propylene oxide) rubber is a sulfur-curable, unsaturated polymer obtained by using allyl glycidyl ether (AGE) as a comonomer. The discovery of epichlorohydrin (ECH) elastomers was announced in 1965.[2] One is the amorphous homopolymer of epichlorohydrin and the other is a 1-to-1-mole copolymer of epichlorohydrin and ethylene oxide (EO). Both polymers contain no unsaturation. Properties have been described by Willis et al.[3] In general, propylene oxide (PO)-based rubber has exceptional low-temperature flexibility, excellent dynamic properties, but moderate oil resistance. Epichlorohydrin-based rubbers have excellent solvent and oil resistance and excellent aging properties.

We have prepared homopolymer of ECH, copolymers of ECH–EO, ECH–PO, and ECH–AGE as well as PO–AGE and terpolymers of ECH–EO–AGE and ECH–PO–AGE with a catalyst system described elsewhere.[4] In this report, a summary of properties of these new elastomers is presented.

EXPERIMENTAL

All experimental rubbers were prepared with one single catalyst consisting of triisobutylaluminum, zinc acetylacetonate, and water. This catalyst is very active and versatile for the polymerization of alkylene oxide. The de-

velopment of this catalyst as well as the polymerization processes are discussed in a separate article.[4] Unsaturated rubbers were prepared by the incorporation of allyl glycidyl ether as co- or termonomer.

The standard recipes used to evaluate saturated homopolymers, saturated copolymers, and unsaturated copolymers and terpolymers are shown in Tables I, II, and III.

TABLE I
Curing Recipe for Epichlorohydrin Homopolymer

	Parts
Rubber	100
IRB No. 2 black	30
Dyphos	5
AgeRite resin D	1
NA-22	1.5
Temperature, °F	307
Time, min	30

TABLE II
Curing Recipe for Saturated Copolymers of Epichlorohydrin and Alkylene Oxide

	Parts
Rubber	100
IRB No. 2 black	30
Red lead	5
Zinc stearate	1
NA-22	1.5
NBC	1
Temperature, °F	307
Time, min	30

TABLE III
Curing Recipe For Unsaturated Copolymers and Terpolymers

	Parts
Rubber	100
IRB No. 2 black	50
Zinc oxide	3
Stearic acid	1
AO 2246	0.5
Sulfur	0.8
Monex	0.55
Temperature, °F	307
Time, min	30

The ingredient sources are listed in Table IV.

TABLE IV
Ingredient Sources

Zinc oxide—New Jersey Zinc Company
Stearic acid—Columbian Carbon Company
Dyphos (dibasic lead phosphite)—National Lead Company
AgeRite Resin D (polymerized trimethyldihydroquinoline)—R. T. Vanderbilt Company, Inc.
NA-22 (2-mercaptobenzothiozole)—E. I. du Pont de Nemours & Co.
Red lead—National Lead Company
NBC (nickel dibutyl dithiocarbamate)—E. I. du Pont de Nemours & Co.
Monex (tetramethylthiuram monosulfide)—Uniroyal Chemical Co.
AO 2246 (2,2′-methylenebis(4-methyl-6-*tert*-butylphenol)—American Cyanamid
Sulfur—C. P. Hall Company

TABLE V
Evaluation Results of Saturated Rubbers

	ECH (100)	ECH-PO (70–30)	ECH-EO (70–30)
Physical Properties			
Compression set, %	25 (20)[a]	20	15 (15)[a]
200% Modulus, psi	1610 (1100)	680	1660 (870)
Tensile, psi	2670 (1580)	1230	2890 (1920)
Elongation, %	405 (545)	385	400 (470)
Crescent tear, lb/in. at 200°F	185 (135)	90	60 (60)
ΔT, °F	69 (59)	76	52 (46)
Perm. set, %	5.7 (2.2)	3.1	0.9 (0.5)
Resilience, %	56.9 (54.4)	57.4	65.8 (72.4)
Shore A hardness	90 (75)	64	85 (62)
Gehman freeze point, °C	−31 (−31)	−46	−46 (−47)
Swell After 7 Days at Room Temperature, %			
Toluene	132 (168)	272	142 (179)
n-Hexane	1.3 (1.1)	18	3 (4)
Acetone	214 (230)	211	171 (170)
Water	1.8 (2.5)	7.2	13 (14)
Ethyl acetate	223 (252)	253	185 (194)
Trichloroethylene	91 (121)	296	157 (226)
H_2SO_4 (2%)	1.9 (2.1)	4.3	14 (13)
NaOH (10%)	0.9 (1.0)	3.0	2.5 (3.1)
Ethyl alcohol	5.6 (6.5)	33	12 (17)

[a] Typical amorphous samples.

RESULTS AND DISCUSSION

Saturated Homopolymer and Copolymers

These samples were compounded with 30 parts carbon black. The experimental homopolymer of epichlorohydrin (ECH) and epichlorohydrin–

TABLE VI
Effects of Variable Allyl Glycidyl Ether (AGE) on Properties

	ECH–PO–AGE weight ratio						
	96–0–4	94–0–6	92–0–8	80–18–2	80–16–4	80–14–6	80–12–8
Physical Properties							
Compression set, %	62	40	32	70	47	30	25
200% Modulus, psi	1500	1850	1900	1800	1200	1500	1500
Tensile, psi	2650	2800	3000	2200	2530	2900	2900
Elongation, %	460	390	330	550	480	460	435
Crescent tear, lb/in. at 200°F	245	385	210	110	350	335	270
ΔT, °F	115	98	92	—	110	82	81
Perm. set, %	21	6.1	6.4	—	17	2.9	1.6
Resilience, %	45	44	42	43	40	41	42
Shore A hardness	95	94	93	95	92	91	87
Gehman freeze point, °C	−32	−32	−32	−34	−34	−34	−34
Swell After 7 Days at Room Temperature, %							
Toluene	111	118	127	216	202	188	193
n-Hexane	1.4	1.7	1.9	5.7	5.5	5.5	5.3
Acetone	168	155	173	284	231	206	205
Water	3.0	2.3	2.3	2.8	2.7	2.8	2.9
Ethyl acetate	170	173	185	278	257	208	213
Trichloroethylene	84	93	101	186	180	170	178
H_2SO_4 (2%)	1.4	1.6	1.5	2.1	2.0	1.9	2.2
NaOH (10%)	5.1	5.8	6.3	10	9.9	9.8	10

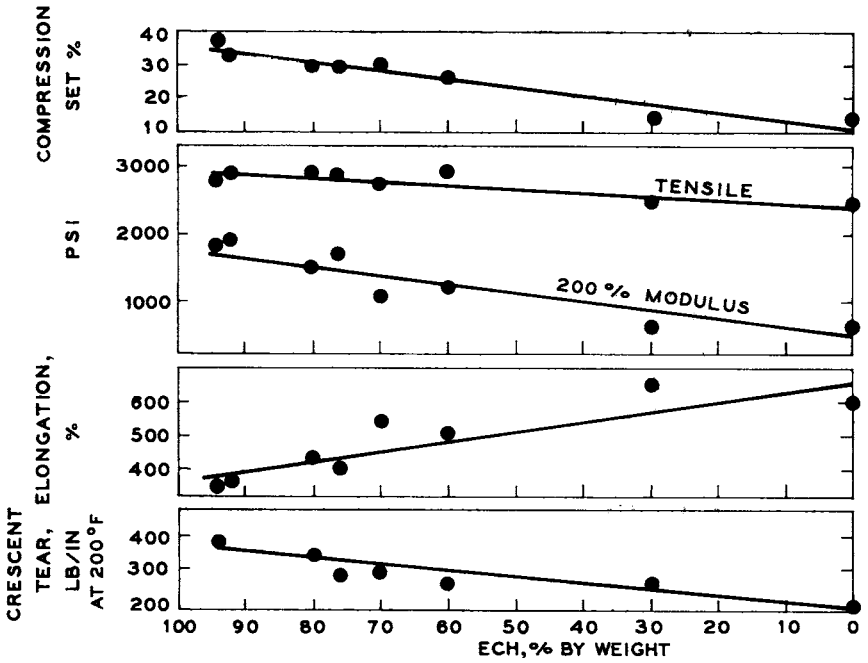

Fig. 1. Effects of variable ECH in ECH–PO–AGE terpolymer-A.

ethylene oxide (ECH–EO) copolymer contain considerable amounts of crystalline polymer,[4] and these rubbers gave significantly better tensile properties, slightly better solvent resistance, but much higher hardness than the "essentially wholly amorphous homopolymer and copolymer" described by Vandenberg.[5] The epichlorohydrin–propylene oxide (ECH–PO) copolymer had poorer overall properties. Evaluation results are shown in Table V.

Unsaturated Copolymers and Terpolymers

The amount of unsaturation in the elastomer is directly controlled by parts of allyl glycidyl ether (AGE) used in the polymerization recipe. Copolymers and terpolymers were prepared and evaluated (Table VI). It is apparent from this evaluation six parts of the ether is sufficient for preparing unsaturated elastomers with good properties.

The epichlorohydrin content in the ECH–PO–AGE polymer can be varied from a ratio of 94–0–6 to 0–94–6. The last one, in reality, is poly(propylene oxide) rubber. A total of eight samples were prepared and compared directly as to physical properties and swelling tests (Figs. 1, 2, and 3).

Vulcanizates of terpolymers, particularly those with high epichlorohydrin content, had rather high Shore A hardness. However, these samples were compounded with 50 parts carbon black. Subsequent evaluation showed that tensile, elongation, compression set, and resilience increased while hardness and heat build-up were largely reduced by lowering the black level (Fig. 4).

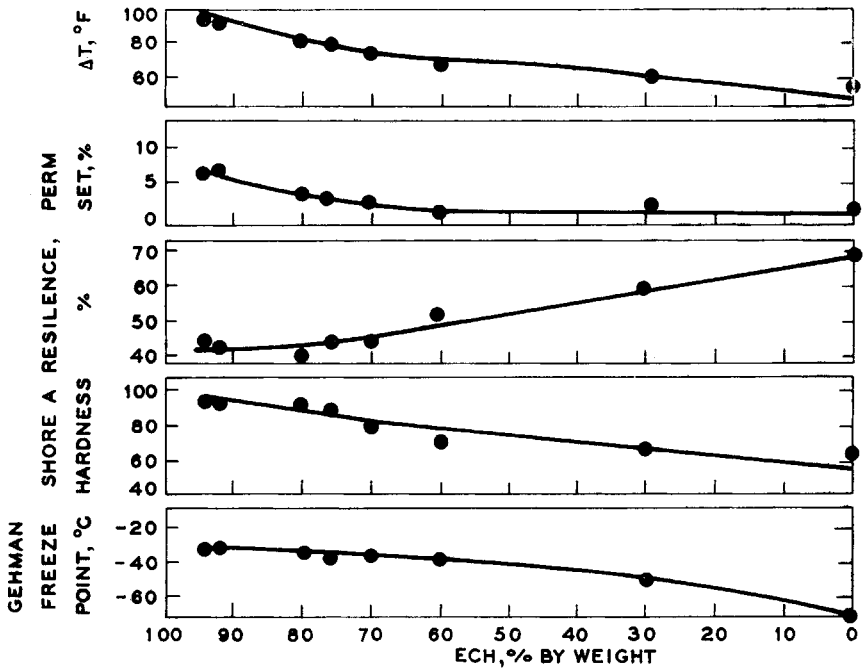

Fig. 2. Effects of variable ECH in ECH–PO–AGE terpolymer-B.

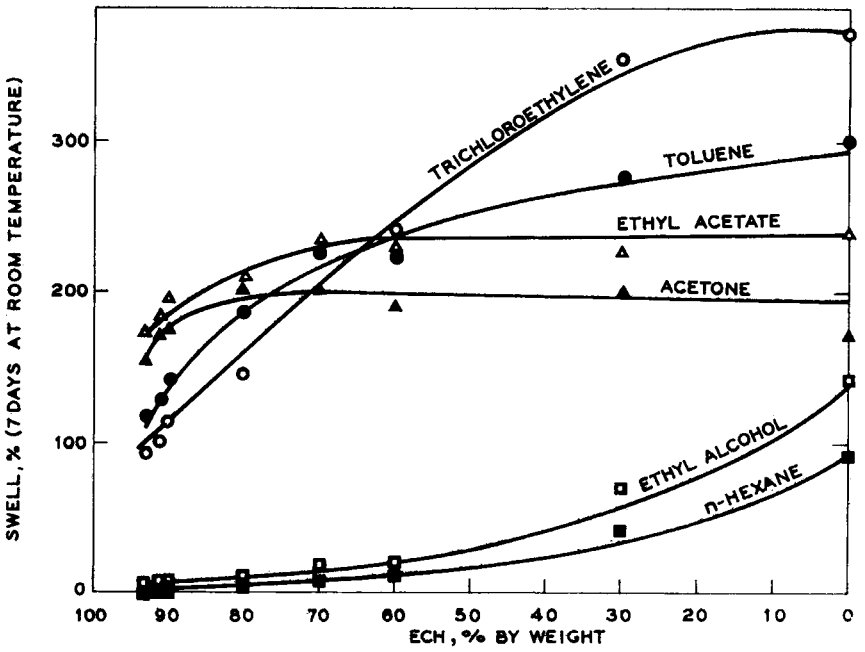

Fig. 3. Solvent resistance of ECH–PO–AGE terpolymers with variable ECH levels.

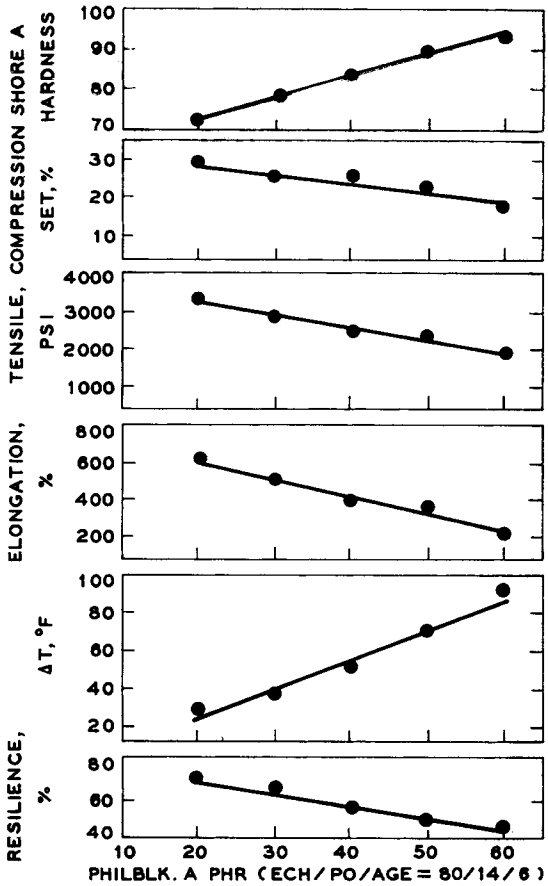

Fig. 4. Effects of carbon black level on properties of ECH–PO–AGE terpolymers.

Terpolymers containing ethylene oxide (EO) gave slightly better stress–strain properties, better solvent resistance, except in water, acid or alkali, and lower Gehman freeze point than the terpolymer containing propylene oxide (Table VII). The vulcanizates of ECH–EO–AGE (70–24–6) terpolymer has tensile properties (ambient and hot) and solvent resistance equal to those of ECH–AGE copolymer, and yet hardness is equal to that of the ECH–PO–AGE terpolymer having 70 parts epichlorohydrin, and freeze point is equal to that of a terpolymer having only 50 parts. In short, it has the best balance of properties of any of the many possible comonomer and termonomer combinations. Even better properties were obtained when 30 parts black were used.

CONCLUSION

The saturated epichlorohydrin rubbers do not give properties as good as those of the sulfur-curable, unsaturated elastomers containing copolymer-

TABLE VII
ECH–EO–AGE Terpolymers Versus ECH–PO–AGe Terpolymers

	ECH–PO–AGE 80–14–6	ECH–EO–AGE 80–14–6	ECH–PO–AGE 70–24–6	ECH–EO–AGE 70–24–6
Physical Properties				
Compression set, %	29	32	30	17 (13)[a]
200% Modulus, psi	1500	1600	940	1500 (1000)
Tensile, psi	2900	3100	2750	3750 (3900)
Elongation, %	430	305	570	450 (570)
Crescent tear, lb/in. at 200°F	335	390	295	405
ΔT, °F	81	83	74	72 (43)
Perm. set, %	2.9	2.7	2.1	1.1 (0.9)
Resilience, %	41	49	45	55 (69)
Shore A hardness	91	92	80	80 (70)
Gehman free point, °C	−32	−43	−34	−47
Swell After 7 Days at Room Temperature, %				
Toluene	188	137	227	153
n-Hexane	5.5	2.8	10	3.4
Acetone	206	157	202	154
Water	2.8	4.4	3.7	11
Ethyl acetate	208	188	237	172
Trichloroethylene	170	139	237	181
H_2SO_4 (2%)	1.9	3.6	2.6	21
NaOH (10%)	1.8	2.1	2.5	4.3
Ethyl alcohol	9.8	9.6	17	15

[a] 30 Parts IRB No. 2 black instead of the standard recipe, which uses 50 parts black.

ized allyl glycidyl ether with or without propylene or ethylene oxide as a termonomer. The vulcanizates of these latter rubbers provided variations of properties, freeze point, hardness, and solvent resistances depending upon the type and amount of comonomer. All also have excellent ozone resistance and exceptionally low permeability to air and many gases.

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