Kirk-Othmer Encyclopedia of Chemical Technology.

POLYETHERS

Polyether elastomers commercially available today are the result of key developments in the 1950s. It had been predicted that high mol wt polyethers would exhibit interesting physical properties, due to the presence of the oxygen atoms in the polymer backbone, which would impart more flexibility to the polymer chain (1). However, conventional catalysts had been effective only in synthesis of low mol wt polymers of epoxides. When these low mol wt polyethers are synthesized with hydroxyl end groups and the resulting polymer allowed to react with a diisocyanate, a polyether urethane product results (2). Since that time, numerous block copolymers incorporating polyethers with functionalized end groups have been synthesized. These compounds are beyond the scope of this article; herein only high mol wt, commercially important, polyether rubber compounds are discussed.

In 1957, it was discovered that organometallic catalysts gave high mol wt polymers from epoxides (3). The commercially important, largely amorphous polyether elastomers developed as a result of this early work are polyepichlorohydrin (ECH) (4, 5), ECH–ethylene oxide (EO) copolymer (6), ECH–allyl glycidyl ether (AGE) copolymer (7, 8), ECH–EO–AGE terpolymer (8), ECH–propylene oxide (PO)–AGE terpolymer (8, 9), and PO–AGE copolymer (10, 11). The American Society for Testing and Materials (ASTM) has designated these polymers as follows:

The catalysts for these compounds are based on aluminum (Nippon Zeon) or tin (Daiso) (12, 13). The preferred catalysts are trialkylaluminum–water combinations used with or without a chelating agent such as acetylacetone. Except for minor variations, few changes in catalyst composition have been made since it was first formulated.

The early technology for the high mol wt polymers was developed by Hercules, Inc., and licensed to the B. F. Goodrich Co. which began marketing ECH homopolymer, ECH–EO copolymer, and ECH–EO–AGE terpolymer under the trade name Hydrin in 1965. Hercules began marketing similar elastomers in 1966 under the trade name Herclor. Hercules also produced PO–AGE copolymer, Parel 58. Two Japanese companies have been in the polyether elastomer business for many years; Daiso Co., Ltd., (formerly Osaka Soda Co., Ltd.) manufactures three chlorinated, amorphous polyethers (ECH, ECH–EO, and ECH–EO–AGE) under the trade name Epichlomer, and Nippon Zeon Co., Ltd., markets ECH–EO–AGE and ECH–AGE under the trade name Gechron. Nippon Zeon and B. F. Goodrich had been associated in an information exchange program since the early 1950s. Nippon Zeon has also begun producing amorphous ECH homopolymer and ECH–EO copolymer,

Polymer	ASTM designation
ECH	CO
ECH–EO	ECO
ECH–AGE	GCO
ECH–EO–AGE	GECO
ECH–PO–AGE	GPCO
PO–AGE	GPO

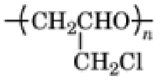
selling these chlorinated elastomers under the Gechron trade name. The company also markets ECH–PO–AGE terpolymers under the Zeospan trademark.

Hercules and B. F. Goodrich are no longer in the polyether manufacturing business. In 1986, Hercules sold its polyether elastomer operation to B. F. Goodrich, which, after operating it for several years, in turn sold it and their whole specialty elastomer division to Zeon Chemicals USA, Inc., in 1989 (14). Zeon Chemicals USA, Inc., is a subsidiary of the Nippon Zeon Co., Ltd. At the present time, manufacture of polyethers is done by Zeon Chemicals in Hattiesburg, Mississippi, Nippon Zeon in Tokuyama, Japan, and Daiso in Mizushima, Japan. Total production is estimated to be 13,000 to 15,000 tons per year.

1. Structure

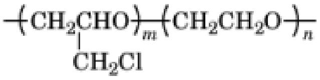
1.1. Epichlorohydrin Elastomers without AGE

ECH homopolymer, polyepichlorohydrin [24969-06-0] **(1)**, and ECH–EO copolymer, poly(epichlorohydrin-*co*-ethylene oxide) [24969-10-6] **(2)**, are linear and amorphous. Because it is unsymmetrical, ECH monomer can polymerize in the head-to-head, tail-to-tail, or head-to-tail fashion. The commercial polymer is 97–99% head-to-tail, and has been shown to be stereorandom and atactic (15–17). Only low degrees of crystallinity are present in commercial ECH homopolymers; the amorphous product is preferred.



$$-\!\left(CH_2\underset{\substack{|\\ CH_2Cl}}{C}HO\right)_{\!n}\!-$$

(1)



$$-\!\left(CH_2\underset{\substack{|\\ CH_2Cl}}{C}HO\right)_{\!m}\!\left(CH_2CH_2O\right)_{\!n}\!-$$

(2)

Crystallinity in ECH and ECH–EO finished products increases over time, and may be detected by x-ray analysis or differential scanning calorimetry. In synthesizing ECH–EO, the process is designed to maximize random monomer sequence and minimize crystallinity. The ECH–EO molecular ratio in these products ranges from approximately 3:1 to 1:1.

1.2. AGE-Containing Elastomers

ECH–AGE, poly(epichlorohydrin-*co*-allyl glycidyl ether) [24969-09-3] **(3)**, ECH–EO–AGE, poly(epichlorohydrin-*co*-ethylene oxide-*co*-allyl glycidyl ether) [26587-37-1] **(4)**, ECH–PO–AGE, and PO–AGE are also amorphous polymers.

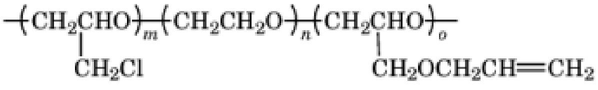
$$-\!\left(CH_2\underset{\substack{|\\ CH_2Cl}}{C}HO\right)_{\!m}\!\left(CH_2\underset{\substack{|\\ CH_2OCH_2CH=CH_2}}{C}HO\right)_{\!n}\!-$$

(3)

Table 1. Commercial Polyether Elastomers

Elastomer	ECH, %	Chlorine, %	Ethylene oxide, %	CAS Registry Number	Specific gravity	ML[a]	T_g, °C
ECH	100	38	0	[24969-06-0]	1.36	40–80	−22
ECH–EO	68	26	32	[24969-10-6]	1.27	40–130	−40
ECH–AGE	92	35	0	[24969-09-3]	1.24	60	−25
ECH–EO–AGE	48–70	24–29	20–50	[26587-37-1]	1.27	50–100	−38
ECH–PO–AGE	40	15	0	[25213-15-4]	1.12	60–80	−48
PO–AGE	0	0	0	[25104-27-2]	1.01	[b]	−62

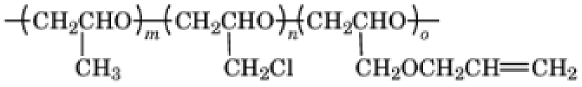
[a] Mooney viscosity at 100°C, ASTM 1646.
[b] Oscillating disk rheometer (ODR) viscosity is 21–26.



$$-\!\left(\mathrm{CH_2\underset{\displaystyle CH_2Cl}{CH}O}\right)_m\!\!\left(\mathrm{CH_2CH_2O}\right)_n\!\!\left(\mathrm{CH_2\underset{\displaystyle CH_2OCH_2CH{=}CH_2}{CH}O}\right)_o\!-$$

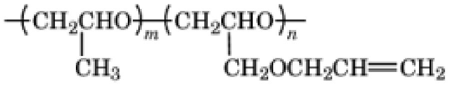
(4)

Crystallinity is low; the pendent allyl group contributes to the amorphous state of these polymers. Propylene oxide homopolymer itself has not been developed commercially because it cannot be cross-linked by current methods (18). The copolymerization of PO with unsaturated epoxide monomers gives vulcanizable products (19, 20). In ECH–PO–AGE, poly(propylene oxide-*co*-epichlorohydrin-*co*-allyl glycidyl ether) [25213-15-4] **(5)**, and PO–AGE, poly(propylene oxide-*co*-allyl glycidyl ether) [25104-27-2] **(6)**, the molar composition of PO ranges from approximately 65 to 90%.



$$-\!\left(\mathrm{CH_2\underset{\displaystyle CH_3}{CH}O}\right)_m\!\!\left(\mathrm{CH_2\underset{\displaystyle CH_2Cl}{CH}O}\right)_n\!\!\left(\mathrm{CH_2\underset{\displaystyle CH_2OCH_2CH{=}CH_2}{CH}O}\right)_o\!-$$

(5)



$$-\!\left(\mathrm{CH_2\underset{\displaystyle CH_3}{CH}O}\right)_m\!\!\left(\mathrm{CH_2\underset{\displaystyle CH_2OCH_2CH{=}CH_2}{CH}O}\right)_n\!-$$

(6)

2. Properties

Properties of the uncompounded elastomers are listed in Table 1 and properties of the compounded polymers in Table 2.

2.1. Epichlorohydrin Elastomers without AGE

The ECH homopolymer has very low gas permeability (two to three times greater than that of butyl rubber), outstanding ozone resistance, good building tack, and low heat buildup. The polymer is flame retardant as a result of its high chlorine content. It has poor resilience at room temperature, but this improves upon heating. The ECH–EO copolymer is less flame retardant due to its lower chlorine content. It has some impermeability

Table 2. Vulcanizate Properties of Polyether Elastomers

Properties	CO	ECO	GCO	GECO	GPCO	GPO
Mooney viscosity at 100°C						
polymer	78	80	62	80	78	72
compound	73	93	60	86	75	83
originals cured at 170°C						
100% modulus, MPa[a]	7.6	5.4	7.2	5.5	5.6	3.4
tensile strength, MPa[a]	16.5	15.0	15.5	15.1	11.4	10.2
elongation, %	225	275	205	280	210	365
hardness, Shore A	74	74	74	73	77	68
air oven aged 70 h at 125°C						
100% modulus, MPa[a]	7.6	5.9	7.5	5.7	0	6.2
tensile strength, MPa[a]	15.3	14.4	13.6	14.7	11.8	10.6
elongation, %	195	240	165	250	80	180
hardness, Shore A	75	72	74	73	90	76
compression set						
70 h at 100°C	13	19	18	19	39	39
70 h at 150°C	58	65	62	66	100	66
brittleness, temp[b]	−20	−40	−24	−40	−46	−61
tear strength, kN/m[c]	32	33	26	35	46	51
ozone resistance, 100 ppm at 49°C, h	>168	>168	>168	>168	>168	>168
volume change 70 h, %						
ASTM fuel A at std[d]	0	0	0	0	12	48
ASTM fuel B at std T	20	17	22	18	65	134
ASTM fuel C at std T	34	32	38	34	106	175
ASTM oil #1 at 125°C	−5	−4	−5	−5	0	11
ASTM oil #1 at 150°C	−4	−5	−4	−5	2	16
ASTM oil #3 at 125°C	5	5	6	5	40	92
ASTM oil #3 at 150°C	6	6	7	6	56	102
water at 23°C	1	6	1	6	3	4
water at 100°C	8	2	10	14	14	10

[a] To convert MPa to psi, multiply by 145.
[b] ASTM 2137.
[c] To convert kN/m to lb/in., multiply by 5.71.
[d] Std T is 23°C.

to gases similar to that of the medium high acrylonitrile rubbers. It has low temperature flexibility to −40°C and exhibits good heat resistance. In contrast with ECH homopolymer, ECH–EO has poor tack.

Vulcanizates of ECH homopolymer and ECH–EO copolymer are resistant to ASTM oils, aliphatic solvents, and aromatic-containing fuels, showing low swell after exposure. The polymers do not harden after exposure to these fluids, although plasticizer may be extracted. Overall, these polymers offer a good balance of heat, ozone, and fuel resistance over a broad temperature range.

2.2. AGE-Containing Elastomers

ECH–AGE copolymer shows excellent ozone resistance and good resistance to softening upon heat aging. The ECH–EO–AGE terpolymers display good ozone resistance with ozone resistance increasing with increasing AGE content. Resistance to softening upon heat aging also increases with increasing AGE content. Like ECH and ECH–EO, vulcanizates of ECH–AGE and ECH–EO–AGE are resistant to ASTM oils, aliphatic solvents, and aromatic-containing fuels. As AGE content of the ECH–EO–AGE terpolymer increases, tensile strength and moduli decrease. Compounding with Group IIA oxides or hydroxides gives the vulcanizates of this terpolymer nitrogen oxide resistance (21). ECH, ECH–EO, ECH–AGE, and ECH–EO–AGE elastomers may be blended; the properties of the blended product are proportional to the amount of each polymer.

Two propylene oxide elastomers have been commercialized, PO–AGE and ECH–PO–AGE. These polymers show excellent low temperature flexibility and low gas permeability. After compounding, PO–AGE copolymer is highly resilient, and shows excellent flex life and flexibility at extremely low temperatures (ca $-65^\circ C$). It is slightly better than natural rubber in these characteristics. Resistance to oil, fuels, and solvents is moderate to poor. Wear resistance is also poor. Unlike natural rubber, PO–AGE is ozone resistant and resistant to aging at high temperatures. The properties of compounded ECH–PO–AGE lie somewhere between those of ECH–EO copolymer and PO–AGE copolymer (22). As the ECH content of the terpolymer increases, fuel resistance increases while low temperature flexibility decreases. Heat resistance is similar to ECH–EO; fuel resistance is similar to polychloroprene. The uncured rubber is soluble in aromatic solvents and ketones.

2.3. Molecular Weight Determination and Solution Behavior

Molecular weight determinations using dilute solution viscosity measurements have been reported for ECH (23, 24). Intrinsic viscosity is related to molecular weight by the Mark-Houwink equation: $[\eta] = KM^a$, where K and a are measured experimentally. The molecular weight is a viscosity average molecular weight, but with the use of the required correction factors, the equation may be used to obtain the number average molecular weight, $\overline{M}_n$, and the weight average molecular weight $\overline{M}_w$, (25). Constants have been determined for amorphous ECH at 100°C in α-chloronaphthalene, and $\overline{M}_w$ may be determined from this relationship: $[\eta] = 8.93 \times 10^{-5}\ \overline{M}_w{}^{0.73}$ (23). A later study of this polymer in α-chloronaphthalene at 25°C gave values of $a = 0.71$ and $K = 8.23 \times 10^{-5}$ dL/g; in tetrahydrofuran at 25°C, $a = 0.80$ and $K = 3.35 \times 10^{-5}$ dL/g (26). When low angle laser light scattering photometry (lalls) is used in conjunction with gel permeation chromatograph (gpc) techniques, M_i values in the eluate may be determined continuously (27, 28). The values obtained using this technique agree with those obtained by dilute solution viscometry (24). Equations relating the sedimentation constant, S, and intrinsic viscosity, $[\eta]$, to molecular weight have been determined for dilute solutions of polyepichlorohydrin in benzene (29):

$$S = 0.145\ M^{0.33}$$

and

$$[\eta] = 0.155 \times 10^{-4}\ M^{0.89}$$

When viscometric measurements of ECH homopolymer fractions were obtained in benzene, the nonperturbed dimensions and the steric hindrance parameter were calculated (24). From experimental data collected on polymer solubility in 39 solvents and intrinsic viscosity measurements in 19 solvents, Hansen (30) model parameters, δ_d and δ_a, could be determined (24). The notation δ_d symbolizes the dispersion forces or nonpolar interactions; δ_a, a representation of the sum of δ_p (polar interactions); and δ_h (hydrogen bonding interactions). The homopolymer is soluble in solvents that have solubility parameters $\delta_d \geq 7.9$, $\delta_p \geq 5.5$, and $0.2 \leq \delta_h \leq 5.0$ (31). Solubility was also determined using a method (32) in which δ represents the solubility parameter and γ the hydrogen bonding parameter. When δ is between 8.6 and 9.8 and the squared hydrogen bonding parameter, γ^2, is between 0.05 and 0.90, the polymer is soluble (31).

Molecular weight determinations of ECH–EO, ECH–AGE, ECH–EO–AGE, ECH–PO–AGE, and PO–AGE have not been reported. Some solution studies have been done on poly(propylene oxide), and these may approximate solution behavior of the PO–AGE copolymer (33, 34).

3. Polymer Preparation

3.1. Epichlorohydrin Elastomers without AGE

Polymerization on a commercial scale is done as either a solution or slurry process at 40–130°C in an aromatic, aliphatic, or ether solvent. Typical solvents are toluene, benzene, heptane, and diethyl ether. Trialkylaluminum–water and trialkylaluminum–water–acetylacetone catalysts are employed. A cationic, coordination mechanism is proposed for chain propagation. The product is isolated by steam coagulation. Polymerization is done as a continuous process in which the solvent, catalyst, and monomer are fed to a back-mixed reactor. Final product composition of ECH–EO is determined by careful control of the unreacted, or background, monomer in the reactor. In the manufacture of copolymers, the relative reactivity ratios must be considered. The reactivity ratio of EO to ECH has been estimated to be approximately 7 (35–37).

The molecular weight of the polymers is controlled by temperature (for the homopolymer), or by the addition of organic acid anhydrides and acid halides (37). Although most of the product is made in the first reactor, the background monomer continues to react in a second reactor which is placed in series with the first. When the reaction is complete, a hindered phenolic or metal antioxidant is added to improve shelf life and processibility. The catalyst is deactivated during steam coagulation, which also removes solvent and unreacted monomer. The crumbs of water-swollen product are dried and pressed into bale form. This is the only form in which the rubber is commercially available. The rubber may be converted into a latex form, but this has not found commercial application (38).

3.2. AGE-Containing Elastomers

The manufacturing process for ECH–AGE, ECH–EO–AGE, ECH–PO–AGE, and PO–AGE is similar to that described for the ECH and ECH–EO elastomers. Solution polymerization is carried out in aromatic solvents. Slurry systems have been reported for PO–AGE (39, 40). When monomer reactivity ratios are compared, AGE (and PO) are approximately 1.5 times more reactive than ECH. Since ECH is slightly less reactive than PO and AGE and considerably less reactive than EO, background monomer concentration must be controlled in ECH–AGE, ECH–EO–AGE, and ECH–PO–AGE synthesis in order to obtain a uniform product of the desired monomer composition. This is not necessary for the PO–AGE elastomer, as a copolymer of the same composition as the monomer charge is produced. AGE content of all these polymers is fairly low, less than 10%. Methods of molecular weight control, antioxidant addition, and product work-up are similar to those used for the ECH polymers described.

4. Processing and Fabrication

All of the polyether elastomers, like other vulcanizable elastomers, can be compounded with processing aids, fillers, plasticizers, stabilizers, and vulcanizing agents to make useful rubber products. A typical compounding recipe for epichlorohydrin elastomer is as follows:

Ingredients	phr
polymer	100
carbon black	70
plasticizer	5
antioxidant	1
processing aid	1
acid acceptor	5
vulcanizing agent	1.5

Table 3. Recipes for Table 2 Vulcanizates, phr[a]

Ingredient	CO	ECO	GCO	GECO	GPCO	GPO
N-762[b]	70	70	70	70	80	80
DOP[c]	5	5	5	5	5	5
stearic acid	1	1	1	1	1	1
NBC[d]	1.4	1.4	1.4	1.4	1.4	1.4
Pb_3O_4, 90%	5.5	5.5	5.5	5.5		
zinc oxide					5	5
ethylenethiourea, 75%	1.5	1.5	1.5	1.5		
MBT[e]					1.5	1.5
TMTM[f]					1.5	1.5
sulfur					1.3	1.3
Total[a]	*184.4*	*184.4*	*184.4*	*184.4*	*196.7*	*196.7*

[a] Column headings indicate the elastomer at 100 phr.
[b] A carbon black designation (see CARBON, CARBON BLACK).
[c] Dioctyl phthalate.
[d] Nickel dibutyl dithiocarbamate., 70%
[e] 2-Mercapto benzothiazole.
[f] Tetramethylthiuram monosulfide.

More specific recipes appear in Table 3. The ingredients are added to the elastomers on standard two-roll mills or in internal mixers. Finished compounds are readily extruded, calendered, or molded in standard equipment. Vulcanization of extrudates is accomplished in live steam autoclaves, liquid salt baths, fluidized beds, and microwave equipment.

For two-roll mixing, a roll temperature between 60–80°C is recommended. Lower temperatures increase the probability of roll sticking, whereas higher temperatures induce scorch and undesirable precure. The elastomer is banded on the mill with the addition of a processing aid. The fillers are added in increments followed by the remaining solid ingredients except the vulcanizing agent. Plasticizers are added after the solids, and the vulcanizing agent is added last with care being taken to ensure that the compound temperature does not rise high enough to cause scorch.

With internal mixers, the elastomer, processing aid, and one-third to one-half of the fillers are mixed, followed by the remainder of the fillers and the other solid ingredients except the vulcanizing agent. Plasticizers should then be added. This first pass mix may be mixed and dropped as high as 175°C to remove moisture. The vulcanizing agent should be added during a second pass with the temperature not exceeding 100°C.

The polyethers are shear sensitive and undergo molecular weight reduction during both mill mixing and internal mixing. This breakdown can be accelerated in the PO–AGE, ECH, and ECH–EO polymers by the addition of an organic peroxide, such as benzoyl peroxide. Since the other polyethers are cross-linkable with peroxides, this technique will not work. The thermoplasticity of the polyethers increases as the mixing temperature increases. This reduces shear and reduces the polymer breakdown. It is extremely important to control the amount of polymer breakdown from batch to batch to control the compound Mooney viscosity and eliminate flow-related problems during subsequent processing.

4.1. Compounding Ingredients

Some common rubber additives can cause problems with the ECH and ECH–EO elastomers. Peroxides cause backbone scission. Acidic materials interfere with most cure systems and can increase polymer degradation during aging. Epoxidized materials, for example, plasticizers, interfere with lead–ethylene thiourea cure systems. Zinc-containing materials may form the Lewis acid zinc chloride, which causes backbone scission during aging of these elastomers as well as the other polyethers containing ECH.

4.1.1. Processing Aids

Stearic acid [57-11-4] or other fatty acids and/or metal soaps of fatty acids are added to reduce shear degradation and mill sticking during mixing. Sorbitan monostearate (ICI's Span 60) is one of the best processing aids to reduce mill sticking.

During some molding and extrusion operations, knit line failures, incomplete mold fill, die drag, and excessive heat buildup, ie, scorch, are problems. Many of these problems are reduced or eliminated by the addition of internal lubricants such as low mol wt polyethylene or Vanfre AP-2 Special, a product of R. T. Vanderbilt.

4.1.2. Fillers

The physical properties of unfilled polyether elastomer vulcanizates are typical of amorphous synthetic elastomers. Tensile strength and hardness tend to be low. Properties are improved by reinforcing fillers (qv) such as carbon blacks, aluminas, and silicas. Reinforcement also is typical. For example, high structure carbon blacks at low loading and silicas yield high tensile strength. Nonreinforcing fillers, calcium carbonate, talc, ground coal, and nonacidic clay are used.

4.1.3. Plasticizers

Addition of plasticizers (qv) to polyether elastomers alters physical properties, improves processing, and can improve low temperature flexibility. Plasticizers also reduce vulcanizate costs by allowing the use of higher levels of less expensive fillers.

The polarity of the polyethers makes them incompatible with hydrocarbon-type plasticizers, which tend to bleed. Effective plasticizers are ethers such as di(butoxyethoxyethyl)formal [143-29-3] (Thiokol's TP-90B), esters such as di(2-ethylhexyl) phthalate [117-81-7] dioctyl phthalate (DOP), polyesters such as Paraplex G50 (Rohm and Haas), and ether–esters such as di(butoxyethoxyethyl) adipate [114-17-3] (Thiokol's TP-95). The lower mol wt plasticizers, DOP, TP-90B, and TP-95 improve vulcanizate low temperature performance. The polymeric plasticizers maintain higher temperature and long-term aging properties. Epoxidized plasticizers should be avoided because they interfere with vulcanization.

4.1.4. Stabilizers and Antioxidants

During the manufacture of the polymers, a hindered phenolic antioxidant is added for protection during storage. Additional antioxidants (qv), such as nickel dimethyldithiocarbamate [15521-65-0], nickel dibutyldithiocarbamate [13927-77-0] (NBC), or 2-mercaptobenzimidazole [149-30-4] are added during compounding to improve air aging and ozone resistance. The hindered phenolics, bis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamoyl)hydrazine and calcium bis-*O*-ethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl) phosphonate provide protection against sour (peroxidized) gasoline. These hindered phenolic materials are ineffective in combination with the nickel dithiocarbamates. Overall aging characteristics of compounds containing the hindered phenolic sour gasoline stabilizers are improved with the addition of AgeRite White.

The principal mechanism of polymer degradation during aging is the acid-catalyzed cleavage of the ether linkage in the backbone. The acid acceptor, a cure activator added as part of the cure system, protects against this mechanism of degradation (41). Some of the more common heat stabilizing acid acceptors are red and white lead oxides, calcium and magnesium oxides, and calcium and barium carbonates (see Heat stabilizers).

4.1.5. Curing Systems

The most commonly used vulcanizing agent for the polyethers not containing AGE, that is, ECH and ECH–EO, is 2-mercaptoimidazoline, also called ethylenethiourea [96-45-7]. Other commercially applied curing agents include derivatives of 2,5-dimercapto-1,3,4-thiadiazole, trithiocyanuric acid and derivatives, bisphenols, diamines, and other substituted thioureas.

In addition to the vulcanizing agent, an acid scavenger that acts as an activator is required. For most of the curatives, a lead-containing compound, such as red lead oxide, litharge, lead phthalate, and lead phosphite, is used most commonly. However, lead-containing materials cause mold fouling during molding operations. This has led to the use of other activators, such as calcium oxide or hydroxide and magnesium oxide for the thiourea curatives. These, and weaker bases such as calcium carbonate and barium carbonate, are used with the dinucleophilic curatives, the dimercaptothiadiazoles and derivatives and trithiocyanuric acid and derivatives. The function of these activators during curing is to scavenge HCl to drive the cross-linking reaction and prevent the HCl from causing backbone cleavage of the polymer.

Although these curative systems may also be used with the polyepichlorohydrin elastomers containing AGE, the polymers were developed to be cured with conventional rubber curatives, sulfur, and peroxides. These polymers containing the pendent allyl group are readily cured with a typical sulfur cure system such as zinc oxide, and sulfur along with the activators, tetramethylthiuram monosulfide [97-74-5] (TMTM) and bis(2,2′-benzothiazolyl)disulfide [120-78-5] (MBTS). A typical peroxide cure system for these elastomers contains sodium or potassium stearate, a peroxide such as dicumyl peroxide, and an unsaturated coagent such as trimethylolpropane trimethacrylate.

Some of the terpolymers containing high levels of AGE give superior sour gasoline and ozone resistance, particularly dynamic ozone resistance. Since the unsaturation is not in the polymer backbone, it can be, and apparently is, sacrificed under sour gasoline or ozone aging. This protection scheme is limited with the peroxide and sulfur cure systems as they involve the allyl functionality of the polymer. The protection is maximized when a dinucleophilic curative, such as trithiocyanurate, is used.

There are no known practical peroxide cure systems for the PO–AGE polymers. Apparently the peroxide attacks the polymer backbone at a rate that is unfavorably competitive with the cross-linking rate. A typical sulfur cure system consists of zinc oxide [1314-13-2], tetramethylthiuram monosulfide (TMTM), 2-2-mercaptobenzothiazole [149-30-4] (MBT), and sulfur. A sulfur donor cure system is zinc oxide, di-*o*-tolylguanidine [97-39-2] (DOTG) and tetramethylthiuram hexasulfide.

5. Economic Aspects

Polyether elastomers are moderately costly when compared with other synthetic rubbers because of their specialty, small-volume nature (Table 4).

Table 4. 1992 Prices for Polyether Elastomers

Elastomer	Cost per kg, $
CO	5.50
ECO	5.40
GCO	5.50
GECO	5.80
GPCO	5.80
GPO	5.10

6. Health and Safety Factors; Toxicity

6.1. Monomers

The monomers used for commercial production of these elastomers are suspected carcinogens. The International Agency for Research on Cancer (IARC) has rated ECH, EO, and PO as probable human carcinogens. Evidence for human carcinogenicity is inadequate for ECH and PO and limited for EO. However, evidence from animal studies is considered sufficient to identify these monomers as potential human carcinogens. The National Toxicology Program (NTP) has found some evidence for carcinogenesis in animal studies involving the inhalation of AGE (42). Studies in human subjects are inconclusive because workers exposed to only one chemical, such as ECH, are not available. Frequently, subjects have been exposed to many chemicals in the course of their employment, and physiological aberrations cannot be attributed to only one factor (43). These monomers, in addition to being potential human carcinogens, also produce acute toxic effects upon exposure. They are harmful when ingested or inhaled, or when skin is contacted. Vapors are extremely irritating to the respiratory tract. Burns result from skin exposure, and EO, ECH, and AGE may cause skin sensitization. AGE, ECH, and PO are absorbed through the skin and may cause systemic toxic effects.

The American Conference of Governmental Industrial Hygenists (ACGIH) has set threshold limit values (TLVs) for airborne concentrations in the workplace (ppm, time-weighted average, 8-h day) as follows: AGE, 5; ECH, 2; EO, 1; and PO, 20 (44). However, the ACGIH has reexamined data on ECH, and has proposed lowering the TLV to 0.1 ppm; it has categorized this monomer as Group A2, a suspected human carcinogen (45).

6.2. Polymers

Studies to determine possible exposure of workers to residual epichlorohydrin and ethylene oxide monomers in the polymers have been done. Tests of warehouse air where Hydrin H and Hydrin C are stored showed epichlorohydrin levels below 0.5 ppm. Air samples taken above laboratory mixing equipment (Banbury mixer and 6″ × 12″ mill) when compounds of Hydrin H or C were mixed gave epichlorohydrin levels below detectable limits, and ethylene oxide levels less than 0.2 ppm, well below permissible exposure limits (46). A subacute vapor inhalation toxicity study in which animals were exposed to emission products from compounded Parel 58 suggests that no significant health effects would be expected in workers periodically exposed to these vapors (47).

6.3. Compounding Ingredients

Ethylene thiourea (ETU), the most commonly used curing agent for epichlorohydrin elastomers, has been determined to be carcinogenic, teratogenic, and goitrogenic in animal studies. One study showed no evidence of cancer or birth defects in humans (48). A study on workers who mixed ETU into masterbatch rubber showed these subjects to have significantly lower levels of thyroxine than process workers or matched controls (49).

To minimize respiratory and skin exposure, ETU is, and should be, used as a dispersion of the powdered ETU in a polymeric binder. Suppliers of dispersions of ETU include Polymerics, Inc., Cuyahoga Falls, Ohio; Rhein Chemie Corp., Trenton, New Jersey; and Synthetic Products Co., Cleveland, Ohio.

The common acid acceptors, red lead oxide and barium carbonate, are both toxic when inhaled or ingested. They are, and should be, used in industry as dispersions in EPDM and ECO. Suppliers of red lead oxide include Polymerics, Inc., Rhein Chemie Corp., and Akrochem Co., Akron, Ohio. Barium carbonate in an ECO binder is available from Rhein Chemie Corp. and Synthetic Products Co.

7. Uses

7.1. Epichlorohydrin Elastomers without AGE

Vulcanizates of ECH homopolymer and ECH–EO copolymer have outstanding ozone and gas permeability resistance. They also retain their flexibility at low temperatures and are fuel resistant. This combination of properties makes them important in automotive applications such as fuel, air, and vacuum hoses, vibration mounts, and adhesives. Homopolymer is used in adhesives because of its natural tack. Used as an additive, ECH–EO copolymer can also impart antistatic properties to plastics. Other industrial applications of these polymers include drive and conveyor belts; hoses, tubing, and diaphragms; pump parts including inner coatings, seals, and gaskets; printing rolls and blankets; fabric coatings for protective clothing; pond liners, and membranes in roofing material.In oil well drilling equipment, uses include drill-pipe protectors, packers, pipe scrubbers, and submersible power-cable jacketing.

7.2. AGE-Containing Elastomers

Modification by addition of a small amount of AGE to the two polymers mentioned above allows for sulfur curing while still maintaining the desirable properties of the original polymers. As ECH levels decrease, fuel resistance also decreases, but this does not present a problem as only small (<10 wt%) levels of AGE are used. ECH–EO–AGE vulcanizates offer excellent heat and ozone resistance, and also excellent compresion set (50). This rubber finds applications in constant velocity boots, mounting isolators, and hose and wire covers. The presence of propylene oxide imparts even greater low temperature flexibility and gas permeation resistance. Thus, ECH–PO–AGE terpolymer and PO–AGE copolymer have outstanding high and low temperature resistance and are used in high flex applications. Both elastomers have good ozone resistance. Although polychloroprene rubbers have good fuel resistance, they do not offer the low temperature flexibility, high temperature resistance, and ozone resistance of ECH–PO–AGE vulcanizates (51). Because of its ECH content, ECH–PO–AGE terpolymer still retains some fuel resistance, whereas the performance of PO–AGE in this area is only fair. Automotive applications of ECH–PO–AGE include dust and fuel hose covers and rubber boots for suspension and transmission systems. This polymer is also used in some automotive anti-vibration applications as well as covering for cable. PO–AGE has vibration damping properties similar to those of natural rubber, but superior heat resistance. It is used in automotive under-the-hood applications such as motor mounts and suspension bushings, where high temperatures preclude the use of natural rubber. Addition of PO–AGE to polycarbonate gives a product that is both impact and chemical resistant (52). When styrene is polymerized with PO–AGE, a product is obtained with better weather resistance than high impact polystyrene (53).

8. Epichlorohydrin Elastomer Derivatives

The principal route of chemical modification of epichlorohydrin elastomers is nucleophilic substitution on the pendent chloromethyl group. Reported nucleophilic substitution products include acetate, glycolate, hydrazine, α-pyrrolidonate (36), azide (54), phosphinyl (55), thiosulfate (56), α-mercaptoacetic acid, thiosalicylic acid (57), thioethers (58), dithiocarbamate (59), isothiouronium (60, 61), imides (62), α,β-unsaturated carboxylic acids (63), cinnamate (64, 65), carbazole (66), and methoxide (67). Preparations of quaternary ammonium salts have also been reported (36, 62, 68–77). Substitution reactions of the pendent chloromethyl group effected by the use of a phase-transfer catalyst have been reported (78). Applications of these modified polyethers include water thickeners (68, 70, 72, 74), breaking emulsions (69), flocculating agents (68), drainage aids in paper manufacture (71), selectively permeable membranes (75, 79), photosensitive material (64, 65, 80), flame retardants (36), and shrinkproofing wool (60).

Modifications of epichlorohydrin elastomers by radical-induced graft polymerization have been reported. Incorporated monomers include styrene and acrylonitrile, styrene, maleic anhydride, vinyl acetate, methyl methacrylate, and vinylidene chloride (81), acrylic acid (82), and vinyl chloride (81, 83, 84). When the vinyl chloride-modified epichlorohydrin polymers were used as additives to PVC, impact strength was improved (83, 84).

BIBLIOGRAPHY

"Elastomers, Synthetic (Polyethers)" in *ECT* 3rd ed., Vol. 8, pp. 568–582, by E. J. Vandenberg, Hercules Inc.

Cited Publications

1. C. C. Price, *Chemist* **38**, 131 (1961).
2. U.S. Pat. 2,866,774 (Dec. 30, 1958), C. C. Price (to University of Notre Dame).
3. E. J. Vandenberg, *J. Polym. Sci.* **47**, 486 (1960).
4. U.S. Pat. 3,158,580 (Nov. 24, 1964), E. J. Vandenberg (to Hercules, Inc.).
5. E. J. Vandenberg, *Rubber Plast. Age* **46**, 1139 (1965).
6. U.S. Pat. 3,158,581 (Nov. 24, 1964), E. J. Vandenberg (to Hercules, Inc.).
7. A. Maeda, *Nippon Gomu Kyokaishi* **53**, 341 (1980).
8. U.S. Pat. 3,158,591 (Nov. 24, 1964), E. J. Vandenberg (to Hercules, Inc.).
9. A. Maeda, *Nippon Gomu Kyokaishi* **61**, 169 (1988).
10. U.S. Pat. 3,728,320 (Apr. 17, 1973), E. J. Vandenberg (to Hercules, Inc.).
11. U.S. Pat. 3,728,321 (Apr. 17, 1973), E. J. Vandenberg (to Hercules, Inc.).
12. T. Nakata, *Nikkakyo Geppo* **41**, 13 (1988).
13. U.S. Pat. 3,766,101 (Oct. 16, 1973), H. Komai and co-workers (to Japanese Geon Co., Ltd. and Osaka Soda Co., Ltd.).
14. E. J. Vandenberg, *Rubber Chem. Technol.* **64**, G56 (1991).
15. K. E. Steller in E. J. Vandenberg, ed., *Polyethers*, American Chemical Society, Washington, D.C., 1975, p. 136.
16. K. E. Steller, *ACS Symp. Ser. 6*, American Chemical Society, Washington, D.C., 1975.
17. H. N. Cheng and D. A. Smith, *J. Appl. Polym. Sci.* **34**, 909 (1987).
18. C. C. Price and M. Osgan, *J. Am. Chem. Soc.* **78**, 4787 (1956).
19. E. E. Gruber, and co-workers *Ind. Eng. Chem. Prod. Res. Dev.* **2**, 199 (1963).
20. E. J. Vandenberg and A. E. Robinson in E. J. Vandenberg, ed., *Polyethers*, American Chemical Society, Washington, D.C., 1975, p. 101.
21. Jpn. Kokai Tokkyo Koho JP 58 002,344 (Jan. 7, 1983), (to Osaka Soda Co., Ltd.).
22. A. Maeda and M. Inagami, *Rubber & Plastics News*, 42 (1987).
23. E. J. Vandenberg in W. J. Bailey, ed., *Macromolecular Synthesis*, Vol. **4**, John Wiley & Sons, Inc., New York, 1972, p. 49.
24. H. Balcar and V. Bohackova, *Collect. Czech. Chem. Commun.* **42**, 2145 (1977).

25. E. Schröder, G. Müller, and K.-F. Arndt, *Polymer Characterization*, Hanser Publisher, New York, 1989, p. 94.
26. H. Balcar and J. Polacek, *Collect. Czech. Chem. Commun.* **41**, 2519 (1976).
27. H. Li and co-workers, *Eur. Polym. J.* **25**, 1065 (1989).
28. D. Chen and co-workers, *Certif. Ref. Mater., Proc. ISCRM 89*, Int. Acad. Publ., Beijing, People's Republic of China, 1989, p. 183.
29. L. S. Yasenkova and co-workers, *Vysokomol. Soedin. Ser. B* **13**, 366 (1971).
30. C. M. Hansen, *J. Paint Technol.* **39**, 104 (1967).
31. J. Kozakewicz and P. Penczek, *Angew. Makromol. Chem.* **50**, 67 (1976).
32. E. P. Lieberman, *Off. Dig. Fed. Paint Var. Prod. Clubs* **34**, 32 (1976).
33. G. Allen, C. Booth, and M. N. Jones, *Polymer* **5**, 195 (1964).
34. G. Allen, C. Booth, and C. Price, *Polymer* **8**, 397 (1967).
35. E. J. Vandenberg, *Pure Appl. Chem.* **48**, 295 (1976).
36. T. N. Kuren'gina, L. V. Alferova, and V. A. Kropachev, *Vyskomol. Soedin. Ser. A* **11**, 1985 (1969).
37. U.S. Pat. 3,313,743 (Apr. 11, 1967), L. J. Filar and E. J. Vandenberg (to Hercules, Inc.).
38. U.S. Pat. 3,634,303 (Jan. 11, 1972), E. J. Vandenberg (to Hercules, Inc.).
39. U.S. Pat. 3,776,863 (Dec. 4, 1973), K. Shibatami and S. Nagata (to Kuraray Co. Ltd.).
40. U.S. Pat. 3,957,697 (May 18, 1976), R. K. Schlatzer (to B. F. Goodrich Co.).
41. J. Day and W. W. Wright, *Br. Polym. J.* **9**, 66 (1977).
42. K. B. Chansky, ed., *Suspect Chemicals Sourcebook: A Guide to Industrial Chemicals Covered Under Major Federal Regulatory and Advisory Programs*, Roytech Publications, Inc., Burlingame, Calif., 1991.
43. L. Hagmar and co-workers, *Int. Arch. Occup. Environ. Health* **60**, 437 (1988).
44. *1991–1992 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*, American Conference of Governmental Industrial Hygenists (ACGIH), Cincinnati, Ohio, 1991.
45. *Appl. Occup. Environ. Hyg.* **5**, 629 (1990).
46. *Form Number 4, Material Safety Data Sheet, Hydrin Elastomers, MSDS Number Z0812.89*, Zeon Chemicals USA, Inc., Louisville, Ky., 1989.
47. *Form Number 8, Material Safety Data Sheet, Parel Elastomers, MSDS Number Z1112.89*, Zeon Chemicals USA, Inc., Louisville, Ky., 1989.
48. D. M. Smith, *J. Soc. Occupa. Med.* **26**, 92 (1976).
49. D. M. Smith, *Br. J. Ind. Med.* **41**, 362 (1984).
50. K. Hashimoto and co-workers, *Elastomerics* **119**, 12 (1987).
51. A. Maeda, K. Hashimoto, and M. Inagami, *SAE Technical Paper Series*, 870194, Conf. Code 09796, SAE, Warrendale, Pa., 1987.
52. U.S. Pat. 4,929,676 (May 29, 1990), M. K. Laughner (to The Dow Chemical Company).
53. J. T. Oetzel, *Rubber World* **172**, 55 (1975).
54. U.S. Pat. 3,645,917 (Feb. 29, 1972), E. J. Vandenberg (to Hercules, Inc.).
55. U.S. Pat. 3,660,314 (May 2, 1972), E. J. Vandenberg (to Hercules, Inc.).
56. U.S. Pat. 3,706,706 (Dec. 19, 1972), E. J. Vandenberg (to Hercules, Inc.).
57. U.S. Pat. 3,417,036 (Dec. 17, 1968), E. J. Vandenberg (to Hercules, Inc.).
58. U.S. Pat. 3,417,060 (Dec. 17, 1968), D. S. Breslow (to Hercules, Inc.).
59. T. Nakai and M. Okawara, *Bull. Chem. Soc. Jpn.* **41**, 707 (1968).
60. U.S. Pat. 3,694,258 (Sept. 26, 1972), E. J. Vandenberg and W. D. Willis (to Hercules, Inc.).
61. U.S. Pat. 3,594,355 (July 20, 1971), E. J. Vandenberg and W. D. Willis (to Hercules, Inc.).
62. T. V. Markman, N. A. Mukhitdinov, and M. A. Askarov, *Deposited Doc.* 1974 VINITI 451-74; *Chem. Abstr.* **86**, 121980d (1977).
63. U.S. Pat. 3,415,902 (Dec. 20, 1967), R. A. Hickner and H. A. Farber (to The Dow Chemical Company).
64. Brit. Pat. 1,404,927 (Sept. 3, 1975), (to Mitsubishi Chemical Industries Co., Ltd.).
65. Ger. Offen. 2,124,686 (Dec. 2, 1971), H. Fukutomi and H. Ohotani (to Dainippon Ink and Chemicals, Inc.).
66. T. D. N'Guyen, A. Deffieux, and S. Boileau, *Polymer* **19**, 423 (1978).
67. J. Kelly, W. M. MacKenzie, and D. C. Sherrington, *Polymer* **20**, 1048 (1979).
68. U.S. Pat. 3,403,114 (Sept. 24, 1968), E. J. Vandenberg (to Hercules, Inc.).
69. U.S. Pat. 3,591,520 (July 6, 1971), M. T. McDonald (to Nalco Chemical Co.).

70. C. K. Riew, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **14**, 940 (1973).
71. U.S. Pat. 3,746,678 (July 17, 1973), C. R. Dick and E. L. Ward (to The Dow Chemical Company).
72. U.S. Pat. 3,864,288 (Feb. 4, 1975), C. K. Riew and R. K. Schlatzer (to B. F. Goodrich Co.).
73. E. Bortel and R. Lamot, *Rocz. Chem.* **50**, 1765 (1976).
74. Ger. Offen. 2,540,310 (Apr. 8, 1976), R. K. Schlatzer, Jr., and H. A. Tucker (to B. F. Goodrich Co.).
75. U.S. Pat. 4,005,012 (Jan. 25, 1977), W. Wrasidlo (to the U.S. Dept. of the Interior).
76. E. Pulkkinen and T. Peteja, *Finn. Chem. Lett.* **1**, 22 (1977).
77. J. Stamberg, *Coll. Czech. Commun.* **29**, 478 (1964).
78. T. Nishikubo and co-workers, *J. Polym. Sci., Part A: Polymer Chemistry*, **26**, 2881 (1988) and references contained therein.
79. U.S. Pat. 3,567,631 (Mar. 2, 1971), C. A. Lukach, E. J. Vandenberg, and W. L. Young III (to Hercules, Inc.).
80. U.S. Pat. 3,923,703 (Dec. 2, 1975), H. Fukutana and co-workers (to Mitsubishi Chemical Industries, Ltd.).
81. U.S. Pat. 3,632,840 (Jan. 4, 1972), E. J. Vandenberg (to Hercules, Inc.).
82. U.S. Pat. 3,546,321 (Dec. 8, 1970), H. Jabloner and E. J. Vandenberg (to Hercules, Inc.).
83. Ger. Offen. 2,147,290 (Apr. 13, 1972), F. Wollrab, F. Declerk, and P. Georlette (to Solvay et Cie).
84. F. Wollrab and co-workers, *Polym. Prepr.* **13**, 499 (1972).

General References

85. D. A. Berta and E. J. Vandenberg in A. K. Bhowmick and H. L. Stephens, eds., *Handbook of Elastomers: New Developments and Technology*, Marcel Dekker, Inc., New York, 1988, p. 643.
86. R. W. Body and V. L. Kyllingstad in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, Vol. **6**, John Wiley & Sons, Inc., New York, 1986, p. 307.

KATHRYN OWENS
VERNON L. KYLLINGSTAD
Zeon Chemicals USA, Incorporated

Related Articles

Elastomers, Synthetic, Survey; Acrylic Elastomers; Butyl Rubber; Chlorosulfonated Polyethylene; Ethylene–Acrylic Elastomers; Ethylene–Propylene–Diene Rubber; Fluorocarbon Elastomers; Nitrile Rubber; Phosphazenes; Polybutadiene; Polychloroprene; Polyisoprene; Thermoplastic Elastomers