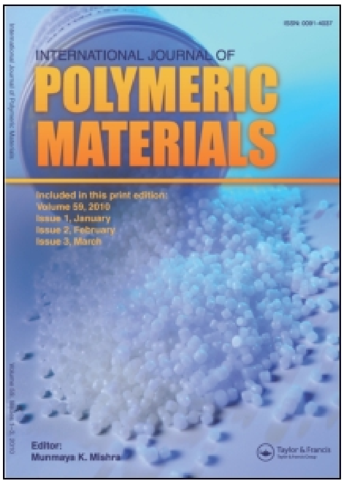

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Degradation and Stabilization of Epichlorohydrin Elastomers

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Degradation and Stabilization of Epichlorohydrin Elastomers

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Thermo-oxidative destruction of epichlorohydrin elastomers by methods of IR- and ESR-spectroscopy. Variation of physico-mechanical properties has been also studied. Antioxidants are proposed for these polymers. The mechanism of oxidation is discussed.

KEYWORDS: Epichlorohydrin elastomers, oxidation, stabilizaers, structure of polymers, mechanical properties, mechanism of degradation

The specialty rubbers are important for modern technologies, conditioning the technical progress in different economical branches. That is because the required conditions are often too drastic and the rubbers for general purposes as natural, isoprene, divinyl, SBR rubbers are not able to satisfy them. Such conditions are: high or very low temperatures, aggressive media (hydrocarbons or other solvents, acids, bases, salts), ionizing radiations, very aggressive climate factors and so on.

The elastomers having a high stability in hydrocarbon media (fuels and mineral oils) constitute a distinct category of specialty rubbers, having important applications in the modern car industry, in oil extraction, in processing, transport and storage of oil products and in other fields of activity.

ASTM D-2000 presents the elastomers classification in point of their thermal and hydrocarbon resistance (Figure 1).[1] It may be observed that the stability in hydrocarbon media devides the elastomers in three groups: low resistant (e.g. natural, SBR, buthyl and EPDM rubbers), medium resistant (e.g. chloroprene rubber, chlorosulphonated polyethylene, ethyl-acrylic and siloxane rubbers) and with high stability (e.g. NBR, epichlorohydrin, acrylate, fluor-siloxane and fluor-carbon rubbers). In each of these groups the elastomers differ by their thermal resistance.

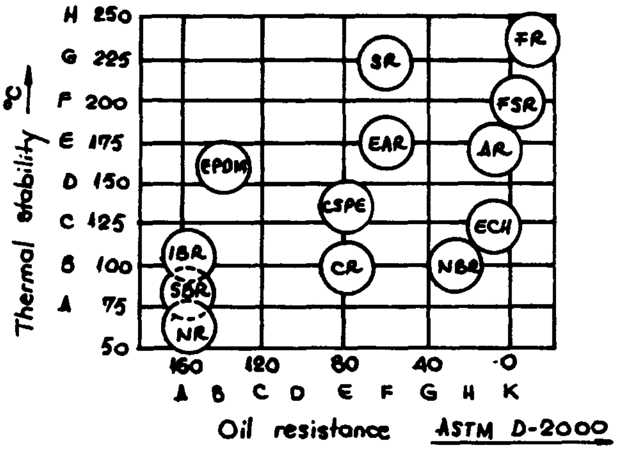


FIGURE 1 ASTM D-2000 rubbers classification. NR—natural rubber; SBR—styrene-butadiene rubber; IBR—isobuthylene-isoprene rubber; EPDM—ethylene-propylene-diene rubber; CR—chloroprene rubber; CSPE—chlorosulphonated polyethylene; EAR—ethyl-acrylic rubber; SR—siloxane rubber; NBR—nitrile rubber; ECH—epichlorohydrin rubbers; AR—acrylic rubber; FSR—fluorsiloxane rubber; FR—fluorine rubber.

The market of hydrocarbon resistant rubbers is characterized by an intense competition. The customers' choice must take into account the achievement of the performance imposed by each particular application field and the rubbers prices, which are strongly rising with the level of properties (Table I).[1]

There are many studies which compare the properties of hydrocarbon resistant elastomers. They show that epichlorohydrin rubbers are competitive, because of their remarkable stability in hydrocarbon media, their good resistance to thermooxidative degradation till 130–135°C and their not very high price. Epichlorohydrin elastomers may be also used as additives to other rubbers, improving the performances of the mixtures.[1-8]

The present work contains some results obtained by the study of epichlorohydrin rubber's thermooxidative degradation.

TABLE I

Relative price indexes of hydrocarbon resistant rubbers

Elastomer	Relative price index
Butadiene-acrylo-nitrile copolymers	1
Epichlorohydrin rubbers	1.7
Acrylic rubber	3.4
Siloxane rubbers	5.1
Fluor-carbon rubber	17
Fluorsiloxane rubber	23

TABLE II

Characteristics of epichlorohydrin elastomer

Specific weight, g/cm^3	1.29
Average viscozimetric molecular weight	600,000
M_W/M_N	2.6
Cristalinity, %	3.5
Glass-transition temperature, °C	−23
Gel content (in CH_2Cl_2), %	4
Humidity, %	0.32
Ashe content, %	1.0
from which Al_2O_3	0.9
Chlorine content, %	38.9

EXPERIMENTAL

Epichlorohydrin elastomer's synthesis was performed by ring-opening polymerization of epichlorohydrin with a preformed catalyst. The polymerization catalyst was obtained from iso$(C_4H_9)_3Al$, diethyl ether and water in toluene solution. The polymerizations were carried out in toluene at 20–60°C, during 3–4 hours.[9] Monomer's concentration was 1.9–2 moles/l and the catalyst's concentration was 42–44 milimoles/l. The characteristics of the polymer are shown in Table II.

For the study of thermooxidative degradation at different temperatures were used stabilized and unstabilized polymer samples. During the thermooxidative destruction, changes in IR spectrum of the polymer occur: some absorbtion peaks decrease and some new peaks appear (Figure 2). The study of degradation kinetics was performed by using the peak of CO-ketonic group at 1720 cm^{-1}, with a Perkin–Elmer 577 spectrometer.

For the stabilization of epichlorohydrin elastomers substances of different classes have been tested (Table III).

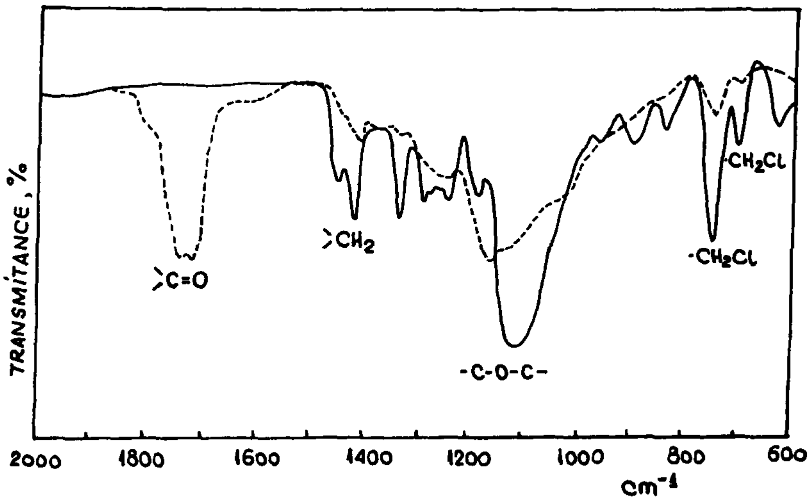


FIGURE 2 IR spectra of epichlorohydrin rubber: ——— before degradation, ---- after degradation.

TABLE III

Stabilizers tested for epichlorohydrin rubber protection

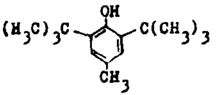
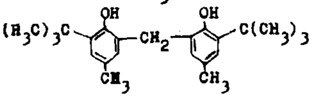
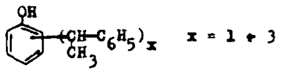
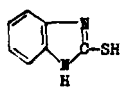
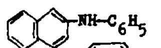
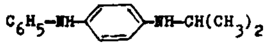
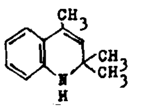
Stabilizer	Chemical structure	Symbol
Topanol OC		OC
2,2'-Methylene-bis(6-tert.buthyl-4-methylphenol		A
Styrene-alkylated phenol		FS
Ronox C	$P(OC_9H_{19})_3$	RC
Mercaptobenzimidazole		MBI
Phenyl-2-naphtylamine		PBN
Wingstay loo		W
Santoflex IP		IP
Poly-(2,2,4-trimethyl-1,2-dihydro-quinoline)		H

TABLE IV

Curing recipes

Constituents, weight parts	Mixtures I_1	I_2	I_3	I_4
Polyepichlorohydrin	100	—	—	—
Herclor C	—	100	—	—
NBR-33	—	—	100	—
Neoprene W	—	—	—	100
Carbon black FEF	50	50	—	—
HAF	—	—	40	—
R300	—	—	—	30
Stearic acid	1.0	0.75	1.0	0.5
Stabilizer H	1.0	1.0	—	—
PBN	—	—	—	2.0
Minium	5.0	5.0	—	—
Zinc oxide	—	—	3.0	5.0
Magnesium oxide	—	—	—	4.0
Ethylenethiocarbamide NA 22	1.5	1.5	—	0.5
Accelerant CZ	—	—	0.7	—
Sulphur	—	—	1.5	—
Curing temperature, °C	160	160	160	160
Curing time, min.	35	45	20	20

The radicalic character of degradation was observed by ESR, using a JES-ME-TX spectrometer which operated in X band.

The properties of cured epichlorohydrin rubber were determined comparatively with NBR having 33% AN, chloroprene rubber (Neoprene W) and epichlorohydrin-ethylene oxide copolymer (Herclor C). The curing recipes are given in Table IV.

RESULTS AND DISCUSSIONS

1. Thermooxidative degradation of unstabilized polyepichlorohydrin

The thermooxidative destruction of unprotected epichlorohydrin rubber was studied at three thermic levels: 120, 150 and 170°C. The kinetic cures, the induction periods and the chlorine content's modification are given in Figure 3 and Table V.

It may be seen that unprotected epichlorohydrin elastomer presents remarkable stability at temperatures at which the stabilized rubbers for general purposes are fastly destroyed. The process isn't determined by breaking of chlorine–carbon bonds: the formation of carbonyl groups is ready at 120°C in about six hours, but the chlorine lost at this temperature represents only 0.1% from the initial content in 16 hours. After 16 hours at 170°C the polymer destruction is very advanced but the chlorine lost represents only 2.5%.

2. The efficiency of different stabilizers

In Table VI are presented the induction periods observed at thermooxidative degradation of stabilized epichlorohydrin rubber at 150°C and at stabilizers concentration 1%. It may be observed that phenolic stabilizers and phosphites are not efficient for polyepichlorohydrin protection. Some of these substances have even a contrary influence, accelerating the degradation. Without efficiency is

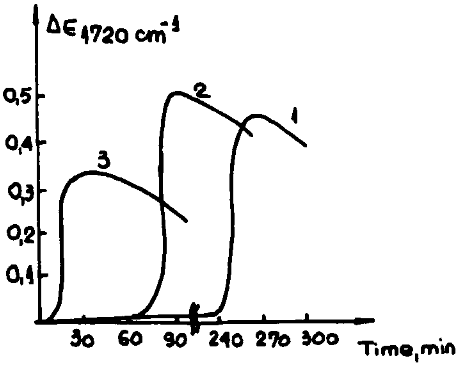


FIGURE 3 Thermaloxidative degradation of unprotected polyepichlorohydrin. Kinetic curves at 120°C (1), 150°C (2), 170°C (3).

TABLE V

Thermooxidative degradation of unprotected ECH rubber

Temperature, °C	Induction period, min	Chlorine lost in 16 hrs, %
120	240	0.10
150	60	0.80
170	8	2.50

TABLE VI

Stabilizer	Induction period, hrs	Relative efficiency
OC	0.5	0.08
A	0.5	0.08
RC	0.5	0.08
—	1.0	—
MBI	1.5	0.25
FS	6.0	1
IP	75	12.5
H	90	15
W	300	50
PBN	330	55

mercaptobenzimidazole too. The stabilizers with secondary amine groups, especially *N,N*-ditolyl-p-phenylenediamine (Wingstay loo) and phenyl-2-naphtylamine have remarkable antioxidant activity.

The polymer protected with amines presents degradation kinetic curves (Figure 4) which show that these stabilizers also produce large propagation periods, suggesting that their oxidation products have yet protecting capacity. Among the tested derivatives, Santoflex IP presented the largest propagation period.

The experimental data suggest that mixtures of stabilizers with secondary amine groups may lead to an increase of stabilization efficiency. This assumption was checked with 1:1 mixtures of Santoflex IP and Wingstay loo, Santoflex IP and PBN, Stabilizer H and PBN, at stabilizer:polymer ratio 1:100. The results

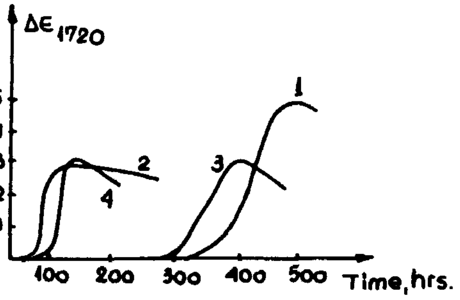


FIGURE 4 Thermaloxidative degradation at 150°C of protected with amines epichlorohydrin rubber 1—PBN 1%; 2—IP 1%; 3—W 1%; 4—H 1%.

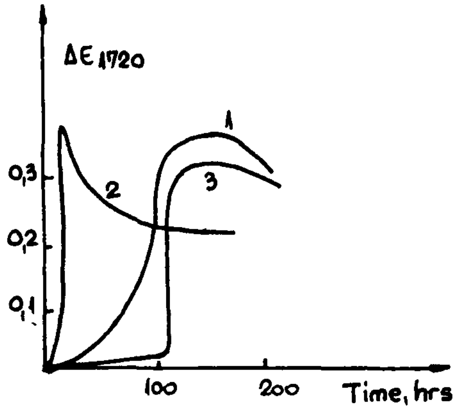


FIGURE 5 Thermaloxidative degradation at 170°C of epichlorohydrin rubber, stabilized with 1% IP + W (1), IP + PBN (2), H + PBN (3).

(Figure 5) proved the high efficiency of IP + W and H + PBN mixtures, which are able to extend the complete periods, of degradation till about 200 hours, at 170°C.

The thermogravimetric data (Table VII) are in agreement with the IR kinetic studies. It may be noticed that there is no weight loss of the samples until 150°C. In the field of 200–350°C, the weight losses rise, reaching 80% for the unprotected polymer and 50–60% for the protected ones.

3. The influence of stabilizers concentration

The kinetics of polyepichlorohydrin degradation was studied at different stabilzer concentrations (Figures 6–8). The results show that Wingstay loo and PBN have normal behavior: by their concentration rise, the induction period of degradation rises. It can be seen also that Wingstay loo assures a good protection at 170°C, but for PBN this thermal level is too high. Santoflex IP is more efficient at 0.7% as at 1% concentration and it may reach Wingstay's loo efficiency at 170°C.

TABLE VII

Thermogravimetric analysis of epichlorohydrin rubber

Temperature, °C	Weight loss, %				
	Unprotected	1% IP	1% W	1% (IP + W)	1% (H + PBN)
50	0	0	0	0	0
100	0	0	0	0	0
150	0	1.0	1.0	1.0	0.5
200	2.0	2.5	1.5	1.5	1.0
250	5.0	4.0	3.0	2.0	3.0
300	13.0	6.5	6.0	4.0	5.5
350	80	53	62	53	58
400	87	89	84	83	82
450	90	92	86	86	86
500	95	95	89	90	90

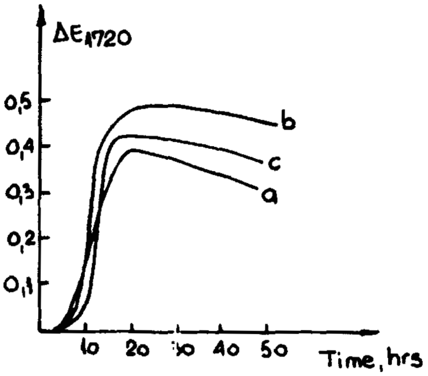


FIGURE 6 Thermaloxidative degradation at 170°C of protected with PBN 0.4% (a), 0.7% (b), 1% (c) epichlorohydrin rubber.

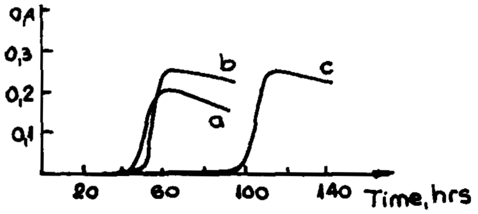


FIGURE 7 Thermaloxidative degradation at 170°C of protected with W 0.4% (a), 0.7% (b), 1% (c) epichlorohydrin rubber.

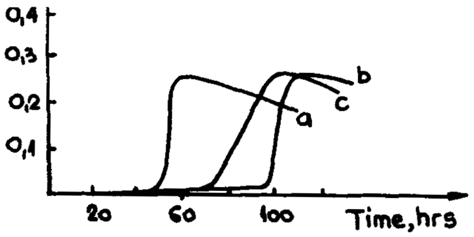


FIGURE 8 Thermaloxidative degradation at 170°C of protected with IP 0.4% (a), 0.7%, (b), 1% (c) epichlorohydrin rubber.

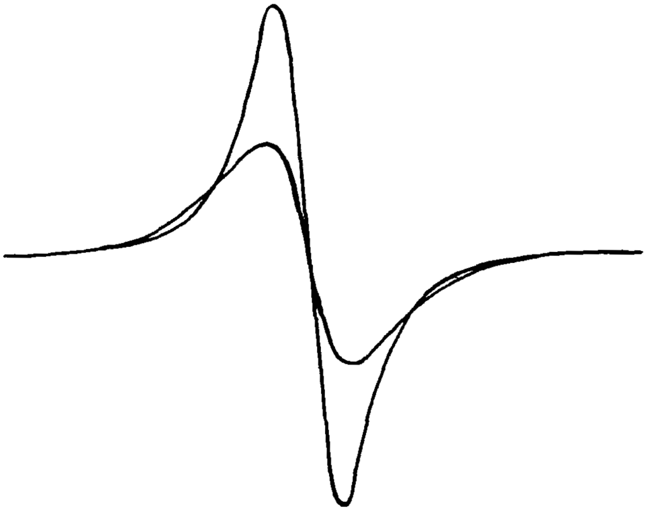


FIGURE 9 ESR spectra of polyepichlorohydrin after 1 hour at 250°C (1) and 350°C (2). H = 3300 ± 50 Gs; Modulati = 2.5 Gs; Frequency = 9.5 GHz; Gain: ×50 (1) and ×1 (2).

TABLE VIII

Mechanical properties of cured rubbers

Mechanical property	I_1	I_2	I_3	I_4
Modulus, Kgf/cm^2				
100% elongation	103	105	—	—
300% elongation	—	—	151	162
Tensile strength, Kgf/cm^2	143	165	189	187
Elongation at break, %	160	180	360	400
Remanent elongation, %	0	0	8	4
Tear strength, Kgf/cm	64	63	85	83
Hardness, °Sh	83	81	71	65
After 3 days at 150°C in air:				
Tensile strength, Kgf/cm^2	114	85	37	82
Elongation at break, %	100	100	50	110

4. The destruction between 250–500°C

ESR study of epichlorohydrin elastomer's destruction at 250–500°C proved the radicalic character of the process and suggest the localization of single electrons at carbon atoms (Figure 9). This fact, nearby the small quantity of chlorine loss indicates a mechanism in which the weak point of the structural unit is the tertiary carbon atom.

5. Properties of cured elastomers

The physical and mechanical properties of epichlorohydrin elastomers are lower than the properties of NBR, Chloroprene and even epichlorohydrin-ethylene oxide rubbers, but after three days at 150°C in air, the properties of epichlorohydrin rubber became superior, because of its better degradation resistance (Table VIII).

Epichlorohydrin elastomer has also higher hydrocarbon resistance as the other studied rubbers, as may be seen in Figures 10 and 11.

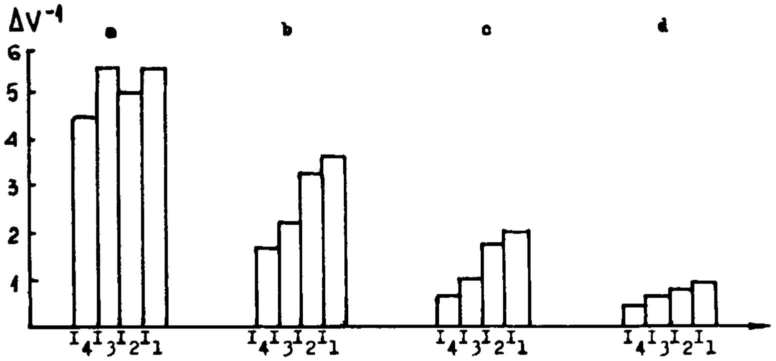


FIGURE 10 The behavior of cured rubbers after 3 days at 40°C in: i-octane (a), i-octane + toluene 7:3 (b), i-octane + toluene 1:1 (c) and toluene (d).

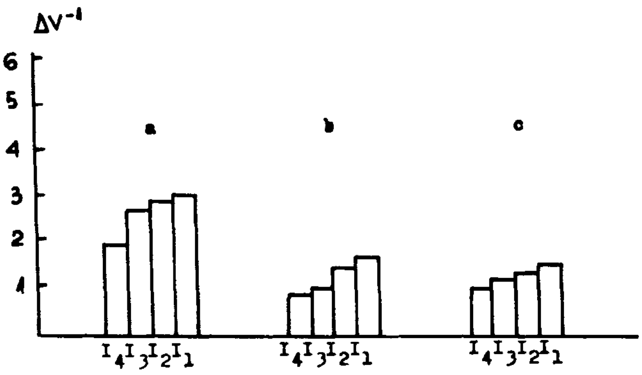


FIGURE 11 The behavior of cured rubbers after 3 days at 40°C in: gazoline (a), gazoline + toluene 1:1 (b) and gazoline + toluene + ethanol 5:3:2 (c).

CONCLUSIONS

The amorphous epichlorohydrin polymers obtained by ionic-coordinated polymerization of epichlorohydrin are characterized by remarkable hydrocarbon resistance and good stability to thermooxidative degradation till almost 150°C.

The thermooxidative stability is considerably improved by the stabilizers with secondary amine groups.

The elimination of chlorine atoms isn't important for the mechanism of epichlorohydrin elastomer's degradation. It seems that the degradation mechanism is dominated by the appearance of free radicals at the tertiary carbon atoms.

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