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SYNTHESIS AND PROPERTIES OF CROSS-LINKED ELASTOMERS BASED ON PR--ETC(U)
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FOREIGN TECHNOLOGY DIVISION



SYNTHESIS AND PROPERTIES OF CROSS-LINKED ELASTOMERS
BASED ON PROPYLENE OXIDE AND DIEPOXIDES

by

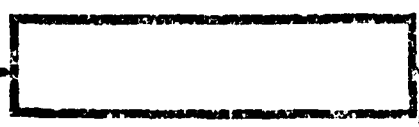
S. G. Soko-cva, L. Ya. Rapport, and O. P. Galanov



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U. S. BOARD ON GEOGRAPHIC NAMES transliteration SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after Ъ, Ь; e elsewhere.
When written as ё in Russian, transliterate as yë or ë.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh
cos	cos	ch	cosh	arc ch	cosh
tg	tan	th	tanh	arc th	tanh
ctg	cot	cth	coth	arc cth	coth
sec	sec	sch	sech	arc sch	sech
cosec	csc	csch	csch	arc csch	csch

Russian	English
rot	curl
lg	log

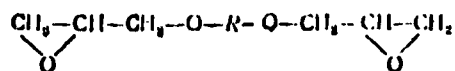
SYNTHESIS AND PROPERTIES OF CROSS-
LINKED ELASTOMERS BASED ON PROPYLENE
OXIDE AND DIEPOXIDES

S. G. Sokolova, L. Ya. Rapport, and
O. P. Galanov.

In recent years new rubber-like polymers possessing a set of valuable technical properties and which are cured by sulfur have been synthesized by means of a joint polymerization of propylene oxide with an unsaturated monoepoxy compound, for example, with allylglycidyl ether [1-3].

It was reported in the patent literature [4-6] that it is possible to accomplish cross-linking of a polymer immediately during the polymerization process by copolymerization of the mono- and diepoxy compounds.

A study was conducted on the effect of the polymerization conditions on the properties on the spatially cross-linked copolymers of propylene oxide with diglycide glycol ethers of the general formula [7]



The presence of two epoxy groups in the diglycide ethers which are capable of opening up during the reaction creates the conditions for a three-dimensional polymerization and cross-linking of copolymers. This makes it possible to manufacture items by means of casting, realizing synthesis of an elastomer directly in the molds without additional curing.

Effect of the copolymerization conditions on the properties of cross-linked propylene oxide and DIEP-1 elastomers.

Content of DIEP-1 in reaction mixture, mole %	Concentration of catalysts in the total number of monomers, mole %	Polymerization conditions		Additional heating conditions		Polymer yield, wt. %	Equiaxial swelling in benzene, Q_p	Vitrification temperature, T_g
		Temperature, °C	Duration, h	Temperature, °C	Duration, h			
1.0	1.05	30	24	—	—	89.5	50.0	—
1.0	1.37	30	42	—	—	95.8	11.0	72.0
1.0	1.37	30	42	50	24	96.1	11.5	—
1.0	1.50	30	42	—	—	94.1	11.6	—
1.0	1.50	30	42	50	24	96.0	9.8	73.5
1.0	1.50	30	42	80	24	94.7	7.7	74.0
2.0	1.05	30	42	—	—	91.0	31.0	—
2.0	1.37	30	42	50	24	95.3	11.5	—
2.0	1.50	30	42	50	24	94.7	9.3	71.0
2.0	1.50	30	42	80	24	93.2	7.6	71.0
3.0	1.50	30	42	80	24	97.0	7.8	—
3.0	1.50	30	42	80	48	94.0	7.2	73.0

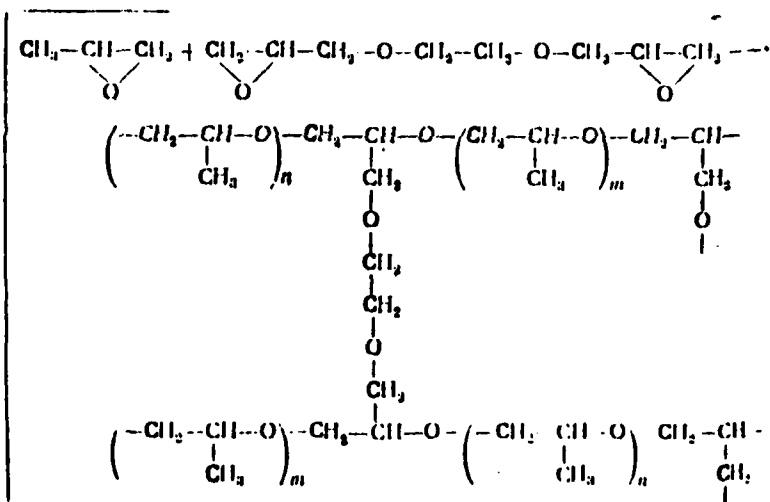
KEY: (a) Content of DIEP-1 in reaction mixture, mole % (b) Concentration of catalysts in the total number of monomers, mole % (c) Polymerization conditions (d) temperature (e) duration, h (f) Additional heating (g) Polymer yield, wt. % (h) Equiaxial swelling in benzene (i) Vitrification temperature

Copolymers were obtained in the presence of a catalytic system - dielectric-water. Technical propylene oxide was treated with potassium hydroxide, desiccated by calcined sodium sulfate, and transferred into the Shlenk's [transliterated] training vessel in a stream of argon. Diglycide ethers of ethyleneglycol (DIEP-1) and diethyleneglycol (DIEP-2), after drying over calcined sodium sulfate, were fractionated in vacuum, removing a fraction 118-119°C/5 mm, in the case of DIEP-1 ($d_4^{20}=1.1332$, $n_D^{20}=1.4542$), and fraction 155-156°C/2-3 mm in the case of DIEP-2 ($d_4^{20}=1.1238$, $n_D^{20}=1.4551$). Diepoxides were stored in the Shlenk vessels in an argon atmosphere. A dielectric synthesized from the zinc powder and ethyl iodide [8] was used as a solution in n-hexane with a concentration of 0.1 g/ml.

Polymerization took place in glass ampules or airtight molds, which were preconditioned in vacuum and washed with argon. The components were immersed in a stream of argon in the following order: propylene oxide (with an appropriate content of water), diepoxide, diethylzinc with a molar ratio of water:dielectric at 0.8:1. After loading, the cooled ampule was unsoldered, shaken, and the temperature was adjusted to the corresponding conditions. Films of cross-linked polymers were obtained using a centrifugal casting technique with

The extent to which the elastomers were cross-linked was estimated on the basis of an equilibrium swelling of polymers in benzene whose coefficient of compatibility with polypropylene oxide $\mu=0.2$ [9]. The cross-linking density characterized by the value of a molecular weight of the chain segment held between two cross links (M_c) was calculated by the method described in literature [10].

The process of cross-linkage formation during the copolymerization of propylene oxide with the diglycidic ethers of glycols can be presented schematically as follows:



During copolymerization the yield of elastomers, in all cases, was over 90% of the weight of the monomer mixture. The vitrification temperature of the obtained elastomers did not differ from that of the linear propylene-oxide rubber ($T_g = -72$ to -74°C). Depending on the conditions of polymerization, the molecular weight of the chain segment between two cross links varied over a wide range ($M_c = 9000$ to 100000).

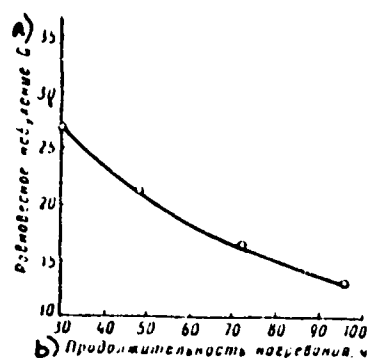


Fig. 1. Variation in the level of cross linkage of copolymers as a function of the heating period (DIEP-1 content - 0.75 mole %, concentration of the catalyst - 1.25 mole %, and temperature - 30°C).

KEY: (a) Equilibrium swelling
(b) Heating period, h

The level of cross linkage of the copolymers can be controlled by varying either the heating duration of the mixture being polymerized with a constant concentration of diepoxide (Fig. 1) or the diepoxide content in the reaction mixture under the temperature-control conditions; the duration of copolymerization is somewhat shortened with a stepped rise of temperature (Fig. 2).

It was established that the level of cross linkage, characterized by the values of equilibrium swelling within the range of 12-17, is optimal for obtaining elastomers with good physical and mechanical indices.

It should be noted that when the DIEP-2 was used, the elastomers had somewhat higher physioco-mechanical indices than in the case of DIEP-1:

	DIEP-1	DIEP-2
Tensile strength, kg/cm ²	70-90	150
Relative elongation, %	600-800	700-900
Permanent elongation, %	20-30	15-20

Cross-linked elastomers based on DIEP-2 are somewhat superior to a nonfilled sulfur vulcanizate SKPO* with respect to the tensile strength and relative elongation, have a lower value of permanent deformation under static compression and a lower brittleness temperature,

* Propylene oxide copolymer with allylglycidyl ether (2 mole %).

while their rebound resilience and TM-2 hardness do not differ from the analogous indices of the SKPO vulcanizates:

	Cross-linked cast elastomer*	Nonfilled SKPO vulcanizate
Stress at 100% elongation, kg/cm ²		
at 20°C.....	10	7
at 100°C.....	0	7
Stress at 300% elongation, kg/cm ²		
at 20°C.....	21	21
at 100°C.....	12	14
Tensile strength, kg/cm ²		
at 20°C.....	177	161
at 100°C.....	24	14
Relative elongation, %		
at 20°C.....	850	690
at 100°C.....	680	460
Permanent elongation, %		
at 20°C.....	18	8
at 100°C.....	12	5
Rebound resilience, %		
at 20°C.....	68	69
at 100°C.....	72	75
TM-2 Hardness.....	51	50
Permanent deformation (20% compression at 100°C), %		
20 h.....	52	77
70 h.....	52	-
Brittleness temperature, °C.....	-73	-62

* DIEP-2 content - 2.0 mole %, catalyst concentration - 1.05 mole %, period during which the temperature was controlled - 24 h at 30°C and 6 h at 60°C, polymer yield - 94.5%, $Q_p=12.2$, $T_c=-73^\circ\text{C}$.



Fig. 2. Variation in the degree of cross linkage of copolymers depending on the content of DIEP-2 in the reaction mixture under various conditions of temperature control (catalyst concentration - 1.05 mole % in total amount of monomers):

- 1 - 24 h at 30°C and 24 h at 60°C;
- 2 - 42 h at 30°C and 6 h at 60°C;
- 3 - 24 h at 30°C and 6 h at 60°C.

KEY: (a) Equilibrium swelling
(b) DIEP-2 content, mole %

The elastomers that were obtained possess good dielectric properties in the frequency range from 400 Hz to 5 kHz; loss tangent - 0.1-0.12; dielectric constant - 3.0-3.5; and temperature of their maximum - 48--55°C.

Thus, a fundamental possibility exists for using the casting method to manufacture articles from propylene-oxide elastomers, which are just as good as the nonfilled sulfur vulcanizates from SKPO with respect to their set of properties.

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