

A New Synthetic Elastomer Based on a Chlorophosphonated Polyolefin

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In recent years the problem of obtaining elastomers for use in applications demanding heat resistance has assumed increasing importance. Thus, rubbers containing little or no unsaturation, such as butyl, Hypalon synthetic rubber, silicone elastomers, and Viton, have moved into the market place.

We are now reporting the preparation of a new, completely saturated synthetic elastomer based on an ethylene-propylene copolymer. Reactive sites for the crosslinking of this elastomer consist of hydrolyzed or alcoholized phosphonyl dichloride groups. The phosphonyl dichloride groups are placed on the copolymer chain by treatment of the polymer with phosphorus trichloride and oxygen, a technique called chlorophosphonation. This reaction has been reported in another paper from this laboratory¹ which discusses chlorophosphonation of polyethylene.

The polyolefin elastomer, when properly compounded with metal oxides, particularly lead oxide, and cured, offers a combination of properties which is unique. The outstanding properties may be summarized as follows:

1. It has excellent heat resistance, being serviceable for extended periods at 155°C. and for short periods up to 200°C.
2. It is completely impervious to attack by ozone.
3. Electrical properties are outstanding and are comparable to those of polyethylene.
4. It is not brittle at -50°C., thus giving it a short-term useful range of 250°C.
5. It has low water absorption.
6. It does not require carbon black for reinforcement.

The purpose of this paper is to outline the preparation and properties of the copolymer, the techniques for chlorophosphonation of the copolymer, and the properties of the vulcanizate.

PREPARATION OF THE COPOLYMER

The ethylene-propylene copolymer used as base stock for the polyolefin elastomer is prepared by a

low pressure process using any one of several organometallic catalyst systems. In order to obtain the best possible base stock, the following requirements must be met: (1) Melt index* should fall in the range 0.1-10; (2) ash content should be less than 0.05%; and (3) the infrared spectrum of the copolymer should contain no bands attributable to polyethylene or polypropylene crystallinity. Polypropylene crystallinity bands appear at 10.3 and 11.9 μ , while a doublet attributed to polyethylene crystallinity appears at 13.73 μ .

The establishment of criteria for melt index, ash content, and crystalline content are extremely important insofar as properties of the vulcanizate are concerned. If melt index falls below 0.1, processability becomes quite difficult. If melt index of the base stock goes above 10, mechanical properties of the vulcanizate deteriorate. High ash contents also result in poor processability.

Crystallinity in the raw copolymer affects the ability of the final vulcanizate to recover from high extensions. With the particular catalyst systems used in this work, copolymers containing from 40 to 90% by weight combined propylene showed none of the bands attributable to polyethylene or polypropylene crystallinity. These bands did appear in the spectra of copolymers which contained less than 40 or more than 90% combined propylene or in spectra of copolymers prepared using certain other catalyst systems regardless of the propylene content. Crystallinity in the copolymer invariably had an effect on vulcanizate recovery after stretching. This effect resulted in higher hysteresis loss and permanent set.

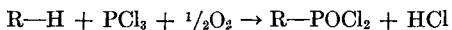
If the criteria just discussed are met, satisfactory base stock can be prepared with facility. In most of our work we have used copolymers containing from 70 to 90% combined propylene.†

* Determined at 190°C. and 44 p.s.i. using melt index tester ASTM #D-1238.

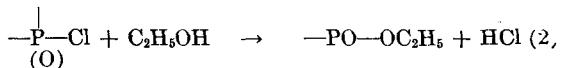
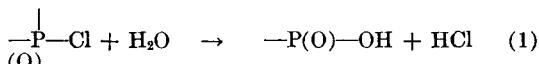
† The amount of combined propylene is determined from the infrared spectrum from the ratio of per cent transmission at the 8.65 μ band and the 13.73 μ band.

THE CHLOROPHOSPHONATION REACTION

Chlorophosphonation, the reaction of aliphatic hydrocarbons with phosphorus trichloride and oxygen, is carried out by passing oxygen through a solution of hydrocarbon (in this case ethylene-propylene copolymer) in either pure PCl_3 or a mixture of PCl_3 and a diluent which itself does not undergo chlorophosphonation.



Polymer is recovered by precipitation in 95% ethanol, a procedure which has been shown to result in approximately 70% hydrolysis [eq. (1)] and 30% alcoholysis [eq. (2)] of the phosphoryl dichloride groups.



In general the chlorophosphonation of ethylene-propylene copolymer has been found to give the best vulcanizates when enough reactive sites are placed on the copolymer chain to give a phosphorus content of 1%. Longer reaction times, however, will result in more phosphoryl dichloride groups and a higher percentage of phosphorus.

The chlorophosphonated product may be vulcanized by a variety of techniques. However, the best results have been found to occur when metal oxides, particularly lead oxide (litharge), are used as crosslinking agents. A typical recipe is 100 parts of chlorophosphonated copolymer, 40 parts of litharge, 3 parts of 2-mercaptobenzothiazole, and 2.5 parts of Staybelite resin. This recipe is the

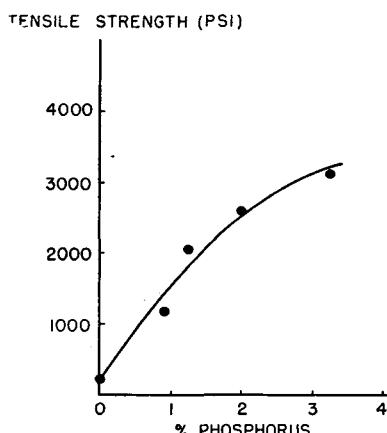


Fig. 1. Per cent phosphorus vs. tensile strength, polyolefin elastomer.

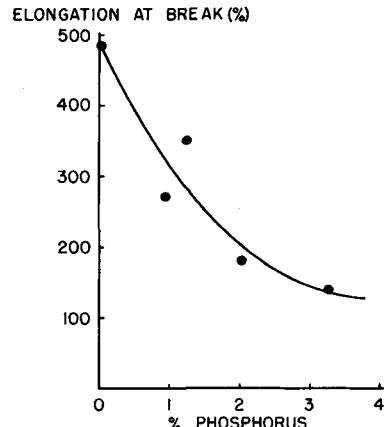


Fig. 2. Per cent phosphorus vs. elongation at break (%), polyolefin elastomer.

TABLE I
Curing Formulations and Conditions

Neoprene	Hypalon	Butyl	Polyolefin elastomer
Neoprene GN	100.00	Hypalon 20	100.00
Stearic acid	0.50	Polyethylene	5.00
Neozone A (anti-oxidant)	2.00	NBC ^a	2.00
Magnesia	4.00	Litharge	1.25
Zinc oxide	5.00	Sulfur	1.50
Semireinforcing black	50.00	Semireinforcing black	Staybelite resin
	161.50	25.00	2.50
		2.00	145.50
		2.00	
		0.50	
		2.00	
		55.00	
			165.75
			153.50

^a NBC is an anti-ozonant, Nickel *N,N*-dibutylthiocarbamate.

same as that used in the curing of Hypalon.² Curing is generally carried out by heating at 155°C. for 30 min.

The tightness of cure in the polyolefin elastomer is determined primarily by the number of phosphonic acid or phosphonic acid ester groups on the copolymer chain. Figures 1 and 2 show the effect on vulcanizate tensile strength and ultimate elongation of the amount of phosphorus in the polymer. From Figure 1 it can be seen that vulcanizate tensile strength may run as high as 3000 p.s.i. with enough phosphorus in the copolymer and with the proper compounding technique.

PROPERTIES OF THE VULCANIZATE

The remainder of this paper discusses physical properties of the polyolefin elastomer. In many of the property measurements we have compared values for the polyolefin-elastomer with those for Hypalon synthetic rubber, butyl rubber, and Neoprene. The formulations and cures of these three commercial materials are arbitrary and it is recognized that other formulations would give different sets of properties. The formulations and curing cycles for each of the four elastomers are given in Table I. The polyolefin elastomer is based on an ethylene-propylene copolymer (90% C₃) which was chlorophosphonated to contain 2% phosphorus.

A. Unaged Stress-Strain Data (Table II)

As indicated earlier in this paper, tensile strength and ultimate elongation of the polyolefin elastomer are functions of the tightness of cure which in turn depends upon the number of phosphonic acid and ester groups attached to the copolymer chain. Tensile strength increases with increasing phosphorus content and ultimate elongation decreases.

TABLE II
Unaged Stress-Strain Data^a

	Neoprene	Hypalon	Butyl	Polyolefin elastomer
Modulus, 100% lb./in. ²	820	510	230	870
200%	1740	1610	440	1630
300%	2560	—	580	—
400%	—	—	950	—
500%	—	—	950	—
Tensile	2845	1975	1120	1630
% elongation	350	235	600	200
% set (at break)	6	6	33	13
Shore creep	76-74	65-59	62-58	66-61
Tear strength, lb.	275	104	151	79

^a Data obtained according to ASTM specifications, ASTM-D412, ASTM-D624 by the Smithers Laboratory of Akron, Ohio.

The elastomer is considerably stiffer than butyl rubber, being lower in extensibility and higher in modulus.

Set at break is fairly high but not so high as in butyl rubber. Tear strength is generally low. This is one of the principal deficiencies of the polyolefin elastomer.

B. Resistance to Heat, Ozone, and Oxygen (Tables III, IV, V, and VI)

The polyolefin elastomer is unaffected by ozone in either a static or dynamic test at an ozone level of 1.5 ppm (Table III). Other tests have shown that ozone concentrations several hundred times greater also have no effect.

Table IV shows that oxygen under pressure does not affect the properties of the polyolefin elastomer after 7 days exposure at 70°C. In an air atmosphere at 155°C. over a 7-day period there is about a

TABLE III^a
Ozone Tests
(Temperature, 100°F. Ozone concentration, 1.5 ppm)

Test #1: Dynamic, 7 days, 0 to 30% elongation

Neoprene: Cracked after 24 hr. and broke at 144 hr.
Butyl: Very few scattered cracks appeared at 144 hr.
Polyolefin: No cracks
Hypalon: No cracks

Test #2: Static under dead weight to afford an elongation of 30%

	Neoprene	Hypalon	Butyl	Polyolefin elastomer
Pounds required to produce 30% elongation	5	2	1.5	5
Elongation at end of test, %	40	40	50	40
Cracking	Complete	None	Slight	None

^a Data obtained by the Smithers Laboratory of Akron, Ohio.

TABLE IV^a
Effects of Oxygen Bomb Aging^b
(7 days, O₂ bomb 300 lb. O₂/70°C.)

	Neoprene	Hypalon	Butyl	Polyolefin
Modulus, lb./in. ²				
100%	1010	690	210	900
200%	1990	1820	400	—
300%	2560	—	520	—
400%	—	—	690	—
500%	—	—	880	—
Tensile	2560	2305	1230	1460
% elongation	300	245	660	170
% set at break	6	9	38	9
Shore creep	80-78	69-64	61-55	68-66
% weight increase	0.42	0.15	0.01	0.06

^a For original properties see Table II.

^b Data obtained by the Smithers Laboratory of Akron, Ohio.

TABLE V^a
Aged-Stress-Strain Data^b
(7 days aging at 155°C. in air oven)

	Neoprene	Hypalon	Butyl	Polyolefin elastomer
Weight loss, %	18	6.2	1.9	0.8
Tensile strength, p.s.i.	No test (brittle)	1300	50	735
% elongation	No test (brittle)	30	1100	90
% set of break	No test (brittle)	3	451	6
% tensile retained	—	66	4.5	45
% elongation retained	—	8.6	470	45
Shore creep	97-97	90-88	41-8	64-62
				ASTM 412, 624

^a For original properties see Table II.

^b Data obtained by the Smithers Laboratory of Akron, Ohio.

TABLE VI
Effect of 200°C. Aging on Various Elastomers

	Natural rubber	Hypalon	Polyolefin elastomer
0 hr. exposure			
% elongation at break	570	500	330
Tensile strength, p.s.i.	811	1159	1015
2 hr. exposure			
% elongation at break	550	430	220
Tensile strength, p.s.i.	28	405	912
4 hr. exposure			
% elongation at break	—	240	220
Tensile strength, p.s.i.	—	353	862
6 hr. exposure			
% elongation at break	—	120	210
Tensile strength, p.s.i.	—	360	756

50% drop in tensile strength and extensibility. Table VI shows the very much shorter time of retention of mechanical properties at 200°C. exposures.

None of the heat aging tests reported in this paper have been determined for polyolefin elastomer containing anti-oxidant. If decomposition of the sample occurs as a result of oxidation at a tertiary carbon atom rather than as a result of the scission of salt bonds, one would expect that anti-

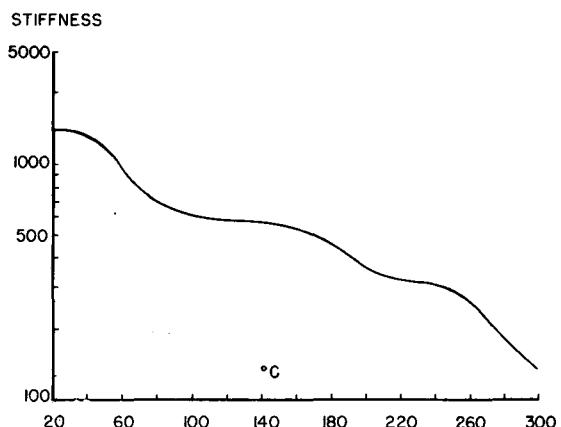


Fig. 3. Stiffness (p.s.i.) vs. temperature, polyolefin elastomer.

oxidants which protect polypropylene would extend the service life of the polyolefin elastomer.

Figure 3 shows the stiffness of the polyolefin elastomer plotted against temperatures ranging from 20 to 300°C. For relatively short periods of time the elastomer is serviceable in the range 250-300°C.

The resistance of the polyolefin elastomer to heat, ozone, and oxygen is its outstanding characteristic. This, in combination with good electrical properties, suggests its use in flexible wire and cable jacketing and insulating applications in which there is a necessity for heat and ozone resistance.

C. Chemical and Solvent Resistance (Tables VIA, VIB, and VIC)

The polyolefin elastomer, basically, is a saturated hydrocarbon. As a result of this basic structure it has poor resistance to aromatic and to chlorinated hydrocarbons. The vulcanizate is not affected by ethylene glycol, monohydric alcohols, and dilute acids and bases. Like Neoprene it is impervious to vegetable oils. Resistance to lubricating oil and to jet fuels is poor.

TABLE VIA^a

Effect of Immersion in ASTM Oil #1^{b,c}
(Properties after 70 hr. immersion at 70°C.)

		Neoprene	Hypalon	Butyl	Poly- olefin elas- tomer
Modulus	100%	790	670	—	—
	200%	1900	—	—	—
	Tensile	2570	1235	200	40
% elongation		250	250	775	160
% set at break		9	13	70	40
Shore creep		41-39	35-34	0-0	20-12
% volume change		+13.3	+24.6	+318	+195

^a For original properties see Table II.

^b ASTM oil #1 is petroleum-base oil with a Saybolt viscosity of 98 sec.

^c Data obtained by the Smithers Laboratory of Akron, Ohio.

TABLE VIB^a

Effect of Immersion in ASTM 0.1 #3^{b,c}
(Properties after 70 hr. immersion at 70°C.)

		Neoprene	Hypalon	Butyl	Poly- olefin elas- tomer
Modulus	100%	250	160	No test	No test
	200%	860	—	—	—
	Tensile	1480	510	Excessive swell	—
% elongation		275	145	—	—
% set at break		29	23	—	—
Shore creep		41-39	35-34	0-0	11-3
% volume change		+40.5	+60.5	+202	+152

^a For original properties see Table II.

^b ASTM oil #3 is a petroleum-base oil with a Saybolt viscosity of 155 sec.

^c Data obtained by the Smithers Laboratory of Akron, Ohio.

TABLE VIC^a

Effect of Immersion in JP4^{b,c}
(Properties after 70 hr. immersion at 25°C.)

		Neoprene	Hypalon	Butyl	Poly- olefin elas- tomer
Modulus	100%	510	270	130	570
	200%	1340	—	—	—
	Tensile	2130	500	290	660
% elongation		305	150	195	120
% set at break		16	19	48	38
% shore creep		54-52	41-38	29-28	59-57
% volume change		+40.5	+60.5	+202	+152

^a For original properties see Table II.

^b JP4 is a jet fuel which consists of 65% gasoline and 35% of a light petroleum distillate.

^c Data obtained by the Smithers Laboratory of Akron, Ohio.

D. Low Temperature Properties

Extensive low temperature property measurements have not been carried out on the polyolefin elastomer. Crude tests have shown, however, that the elastomer is not brittle at temperatures as low as -50°C. Since the elastomer can be used as high as 200°C., the service range, at least for short periods, is 250°C.

E. Electrical Properties

The dielectric properties of the polyolefin elastomer vulcanizates approach those of polyethylene. Table VII compares electrical properties of Hypalon, Neoprene, poly(vinyl chloride) and the polyolefin elastomer.

TABLE VII
Electrical Properties of Various High Polymers

	Poly(vinyl chloride)	Hypalon	Neoprene	Polyethylene	Polyolefin elastomer
Dielectric strength, v./mil.	400-800	400-750	400-600	475	507
Dielectric constant					
1 mc.	2.9			2.3	2.43
60 c.	3.2			2.3	2.46
1 kc.			6.7	2.3	2.46
10 kc.		5-7			
Power factor					
1 mc.	5×10^{-3}			5×10^{-4}	3.1×10^{-3}
60 c.	5×10^{-3}			5×10^{-4}	4.9×10^{-3}
1 kc.		1.9×10^{-2}	2.5×10^{-2}	5×10^{-4}	5.3×10^{-3}
10 kc.				5×10^{-4}	5.1×10^{-3}
Volume resistivity, ohm-cm., 50% R.H.	$10^{14}-10^{16}$	10^{13}		10^{15}	10^{16}
Surface resistivity, ohms, 50% R.H.	5×10^{15}				

References

1. Schroeder, J. P., and W. P. Sopchak, "The Reaction of Phosphorus Trichloride and Oxygen with Polymers," accepted by *J. Polymer Sci.*, subject to revisions.
2. Warner, R. A., *Rubber Age*, **71**, 205 (1952).

Synopsis

A new synthetic elastomer has been obtained based on an ethylene-propylene copolymer prepared using an organometallic catalyst system. Reactive sites (phosphonyl dichloride groups) are placed on the copolymer chain by treating the polymer with phosphorus trichloride and oxygen. After hydrolysis or alcoholysis of the phosphonyl dichloride groups to phosphonic acid or phosphonic acid esters, vulcanization may be carried out by reaction with metallic oxides, particularly lead oxide. Vulcanizates of the polyolefin elastomer have outstanding resistance to heat, ozone, and oxygen, and have excellent electrical properties. This combination suggests the use of this material in high temperature electrical applications.

Résumé

On a obtenu un élastomère synthétique basé sur un copolymère éthylène-propylène, préparé en utilisant un système catalytique organo-métallique. On fixe des sites réactionnels (groupe phosphonyl dichlorure) sur la chaîne du copolymère en soumettant le polymère à l'action du tri-

chlorure de phosphore et de l'oxygène. Après hydrolyse ou alcoolysé des groupements dichlorophosphonyles en acide phosphonique ou en esters phosphonique, on peut opérer la vulcanisation par réaction avec des oxydes métalliques, en particulier, l'oxyde de plomb. Les élastomères polyoléféniques vulcanisés présentent une résistance exceptionnelle à la chaleur, l'oxygène et l'ozone et ont d'excellentes propriétés électriques. Cette combinaison suggère l'emploi de ces substances dans des applications électriques à haute température.

Zusammenfassung

Ein neues synthetisches Elastomeres wurde auf Grundlage eines mit einem organometallischen Katalysatorsystem dargestellten Äthylen-Propylencopolymeren erhalten. Das Copolymer wird durch Behandlung mit Phosphortrichlorid und Sauerstoff mit reaktionsfähigen Stellen (Phosphonyldichloridgruppen) versehen. Nach Hydrolyse oder Alkoholysé der Phosphonyldichloridgruppen zu Phosphonsäure oder Phosphonsäureestern kann durch Reaktion mit Metalloxyden, besonders Bleioxyd, Vulkanisation herbeigeführt werden. Vulkanizate des Polyolefine elastomeren besitzen eine ungewöhnliche Beständigkeit gegen Erhitzen, Ozon und Sauerstoff und haben ausgezeichnete elektrische Eigenschaften. Damit wird die Verwendung dieses Materials für elektrische Zwecke bei hohen Temperaturen nahe gelegt.

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