

## Chlorinated and Chlorosulfonated Polyolefins

P. J. CANTERINO and G. R. KAHLE

*Phillips Petroleum Company, Bartlesville, Oklahoma*

### INTRODUCTION

The recent discovery of the low-pressure polymerization processes for production of polyethylene has made available polyolefins with a wide spectrum of physical properties. The properties of polyethylene are changed by altering the number and length of the side groups which are attached to the main carbon chain of the polymer. Density, crystallinity, rigidity, softening point, and tensile strength are increased as the number of side groups decreases.

Of the many chemical reactions studied for the modification of polyethylene, chlorination and chlorosulfonation have aroused the most interest. Considerable work has been done in these areas.<sup>1-14, 16-20</sup> High-pressure (low-density) polyethylene was used in the earlier studies. The properties of these chlorinated polyethylenes were influenced by the molecular weight of the polymer, degree of chlorination, structure of the chain, and technique used for chlorination. Variation of these factors produced a large number of products with properties ranging from those of soft, pliable elastomers to rigid plastics.

The present work deals chiefly with the change in physical properties of the chlorinated and chlorosulfonated products as the structure of the starting polyethylene or ethylene copolymer is varied.

### DISCUSSION OF RESULTS

#### Effect of Chlorine Content on the Physical Properties

**Comparison of Low- and High-Density Polyethylene.** Although considerable work has been done on the chlorination of low-density polyethylene little physical property data have been reported in the literature. In order to characterize these products two samples typical of low-density polyethylene were chlorinated in solution with carbon tetrachloride. The polyethylenes

used were Alathon-1 from Du Pont and DYNK from Bakelite.

The variation of tensile strength of the products with chlorine content is shown in Figure 1. The tensile strength at first decreases with increase in amount of chlorine along the chain, reaches a minimum at 30-40% Cl, and then increases to values higher than those of the original polymer.

The tensile strength of chlorinated high-density (linear) polyethylene is shown in Figure 2. Phillips' polyethylenes of three different molecular weights were chlorinated in tetrachloroethane solution for this study. In measuring the tensile strength, the stress was applied at 20 in./min. The tensile strength decreases with increasing chlorine content. However, at a chlorine content slightly above 10 wt.-% the two high molecular weight linear polyethylenes show a sharp increase in tensile strength with an optimum at a chlorine content of 20-30 wt.-%. Then the tensile strength decreases once more and a minimum is reached at 35-45 wt.-% Cl. The tensile strength increases rapidly above 45 wt.-% Cl to values higher than those of the parent polyethylene. The chlorinated low-density polyethylene and the chlorinated low molecular weight high-density polyethylene did not show the maximum in tensile strength. It is evident from these curves that, as the molecular weight of the polyethylene was increased, higher values for tensile strength were obtained.

The tensile strength of cold-drawn chlorinated polyethylene is presented in Figure 3. The samples were drawn on the Instron tensile testing machine at the rate of 2 in./min. to an elongation just below the elongation-at-break determined previously. The oriented samples were allowed to stand overnight, and the tensile strength was determined, applying a stress of 12 in./min.

All the chlorinated samples show increased tensile strength caused by orientation except those containing more than about 35 wt.-% Cl. The oriented chlorinated products from linear poly-

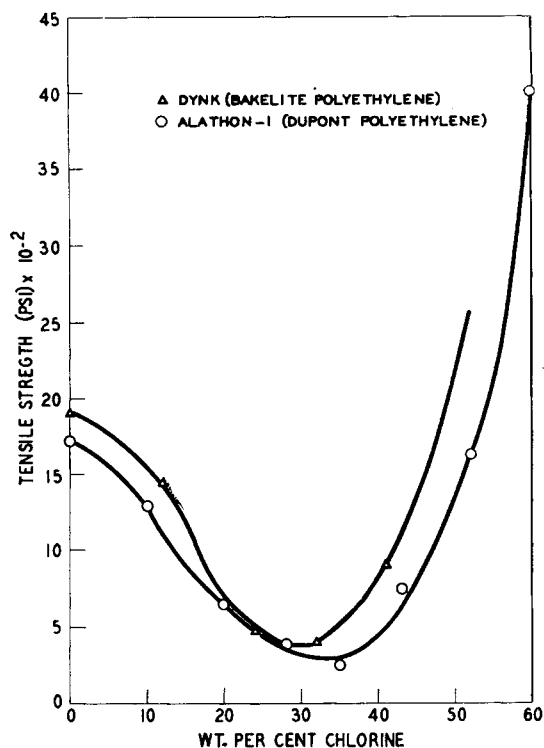


Fig. 1. Tensile strength of chlorinated low-density polyethylene.

ethylene of medium-molecular weight exhibit remarkably high tensile strength below this chlorine content. For this series no orientation occurs at 50 wt.-% Cl, since 100% retraction occurs when the cold-drawn specimen is allowed to relax. Increase in the chlorine content to above 50 wt.-% causes orientation.

Chlorinated high-density polyethylene of low molecular weight shows a slight orientability. Chlorinated Alathon-1 is also oriented to a certain degree by cold drawing. The tensile strengths of these products are much lower than those for the chlorinated, high molecular weight, high-density polyethylene samples.

The maximum in the tensile strength curve and the break observed in the curve of the tensile strength of oriented, chlorinated, high-density polyethylene are attributable to the crystalline nature of the polymer. The molar cohesive forces between the methylene groups in the polymer chains are relatively weak; however, the regular structure of the chains permits a large degree of crystallization to occur resulting in a product of high tensile strength. Introduction of chlorine atoms along the chain alters the geometrical fitting of the chains in the crystal lattice. The noncrystalline areas increase, and the material becomes softer and more flexible. The tensile strength

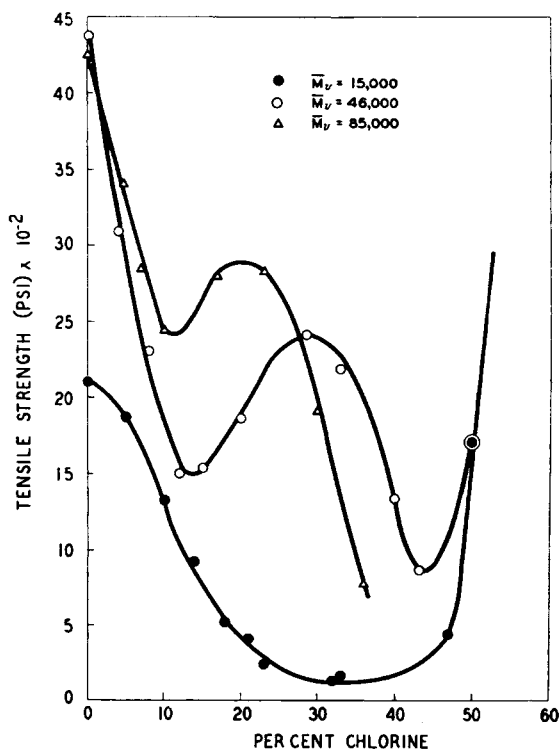


Fig. 2. Tensile strength of chlorinated linear polyethylene.

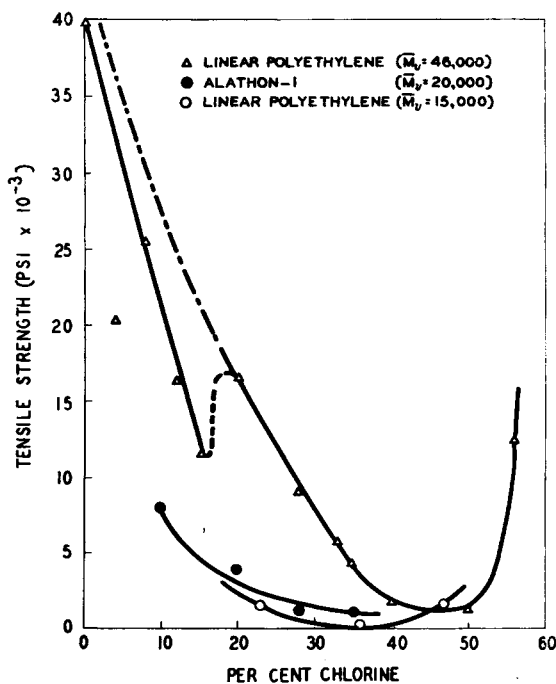


Fig. 3. Tensile strength of cold-drawn chlorinated polyethylene.

decreases with the disappearance of the highly crystalline areas.

In Figure 2 the tensile strength, determined by applying stress at 20"/min., was a function of chlorine content. Under these conditions the chains in the crystalline polymer have little opportunity to uncoil and align themselves in the direction of the stress. The polymer is still partially crystalline in the region where the tensile strength appears to increase with increasing chlorine content (15–35 wt.-% Cl). However, a larger portion of the polymer is now in the amorphous phase. The chains and crystallites are oriented in the direction of the stress, the chains close-pack and Van der Waal's forces come into play. The polymer is crystalline enough with chlorine contents below 15% so that, on application of a rapid stress, the amorphous areas and crystallites do not have the opportunity to orient, and the material fails with a lower stress.

The decrease in tensile strength, which appears at 30 wt.-% Cl and reaches a minimum at 45% Cl is probably a result of the total disappearance of the crystallites. The noncrystalline rubbery material contains enough chlorine atoms along the chains to prevent crystallization, but not enough for their polar attraction to compensate for the loss in crystallinity. As the chlorine content increases to above 50 wt.-%, the polymer becomes "glassy,"

and the chain segments become immobilized by the attraction of the groups on the chains (beyond the second order transition temperature). The material becomes harder, and the tensile strength once more increases.

Because Alathon-1 is less crystalline than the higher density polyethylene, it is already in the crystalline region that is reached by linear polyethylene at about 15 wt.-% Cl. Alathon-1 is sufficiently amorphous so that a rapid stress causes the molecules to uncoil and orient in the direction of the stress. Chlorination to 15 wt.-% Cl further reduces its crystallinity. It does not exhibit the peak in tensile strength which is found in the high-density polyethylene. The high-density, low molecular weight polyethylene does not show this peak because of the low molecular weight. Each chain necessarily is incorporated in fewer crystalline regions. The chains thus can slip past one another more easily on the application of stress, giving rise to plastic flow. At 28 wt.-% Cl both the higher and lower molecular weight linear polyethylenes have high orientation. The Alathon-1 has low orientation. All three samples have low crystallinity at this chlorine content.

Flex temperatures of chlorinated polyethylene are plotted in Figure 4. Flex temperature decreases with increasing chlorine content to 30 wt.-% Cl. Above this concentration it begins to rise. Although the low-density polyethylene originally has a flex temperature lower than product derived from the high-density polymers, at about 20% Cl the curves approach each other. The flex temperature is affected only slightly by the molecular weight of the polyethylene; the higher molecular weight polymers have the higher flex temperatures.

### Copolymers

Polymers from each end of the polyethylene density spectrum were compared in the previous section. Some ethylene copolymers with properties falling between the two extremes were also chlorinated. Table I characterizes the starting materials. The tensile strength of the chlorinated ethylene-1-butene copolymers is shown in Figure 5. The peak in the tensile strength curve is shifted to lower chlorine content with an increase of 1-butene in the polymer. The curve for the chlorinated copolymers with 1.6% combined 1-butene does not differ greatly from the curve of the chlorinated homopolymer. These polymers were low-melt index or high molecular weight resins. The

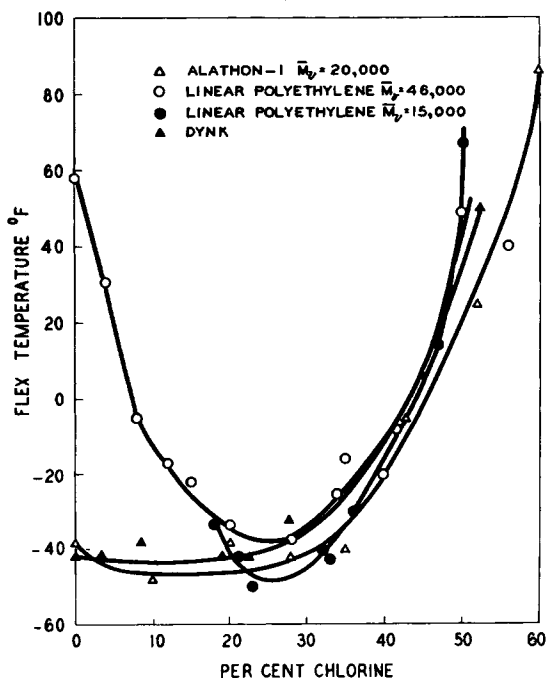


Fig. 4. Flex temperature of chlorinated polyethylene.

TABLE I  
Phillips Ethylene Copolymers

Density	Inherent viscosity	Melt index		Wt.-% comonomer in polymer	
		Standard	High load <sup>a</sup>	C <sub>4</sub> -	C <sub>3</sub> -
0.957	4.008	—	2.50	0.0	0.0
0.948	2.79	0.048	4.05	1.6	—
0.937	2.546	0.14	12.8	4.0	—
0.932	3.555	—	2.8	4.5	—
0.936	1.8	0.79	35.0	5.9	—
0.927	1.9	0.499	30.0	—	6.2

<sup>a</sup> Standard weight 10X (HLMI).

tensile strength of two lower molecular weight copolymers is shown in Figure 6. One,  $[\eta] = 1.9$ , is the ethylene-propylene copolymer, and the other,  $[\eta] = 1.8$ , is a 1-butene copolymer. These two polymers have tensile strength curves similar to the homopolymers and differ from the high molecular weight copolymers. This is not surprising, because higher molecular weight polymer chains take part in more areas of chain entanglement. The entanglements act as side groups when the stress is applied and prevent the flow obtained with the lower molecular weight samples, causing the

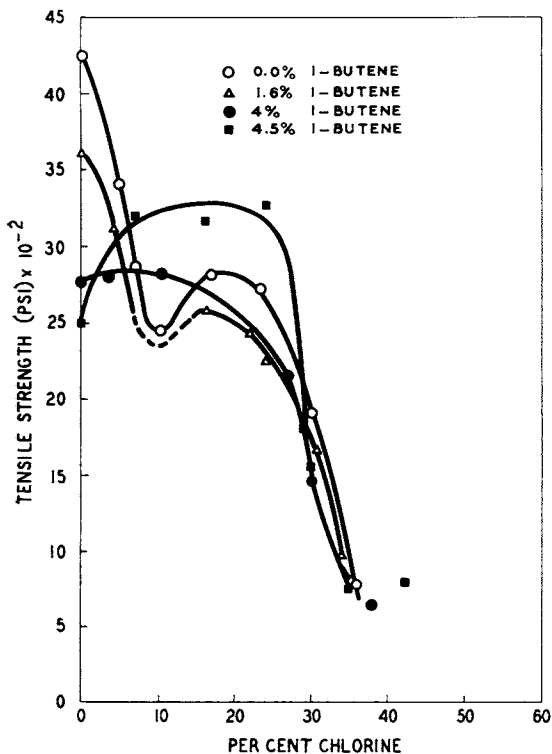


Fig. 5. Tensile strength of butene copolymers.

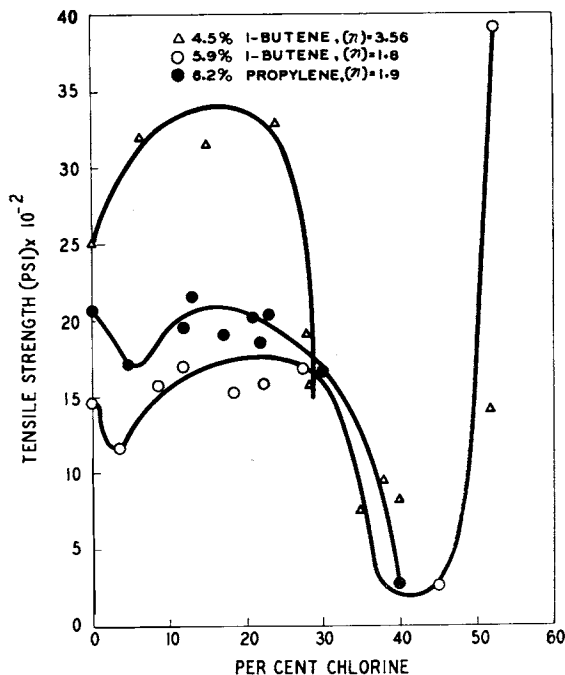


Fig. 6. Tensile strength of lower molecular weight copolymers.

observed shift of the curve of the higher viscosity polymer to the left.

**Other Properties of Chlorinated Polyethylene**

The 100% modulus of some chlorinated ethylene polymers and copolymers is shown in Figure 7. Modulus depends chiefly on the amount of residual crystallinity below 30 wt.-% Cl. The modulus becomes about the same for all the polymers when the crystallinity disappears as a result of chlorination. Above 40 wt.-% Cl the higher molecular weight polymers have a higher modulus.

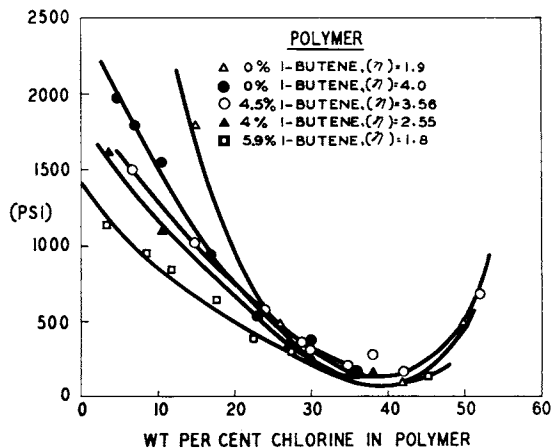


Fig. 7. Variation of 100% modulus with type of polymer.

The zero strength temperatures of the chlorinated polymers depend chiefly on the molecular weight of the polymer (Fig. 8) once the crystallinity dimin-

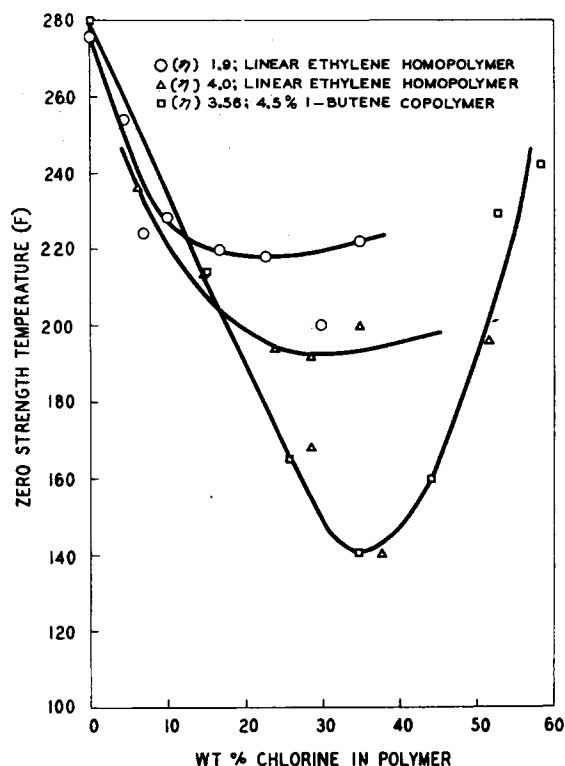


Fig. 8. Variation of zero-strength temperature with type of polymer.

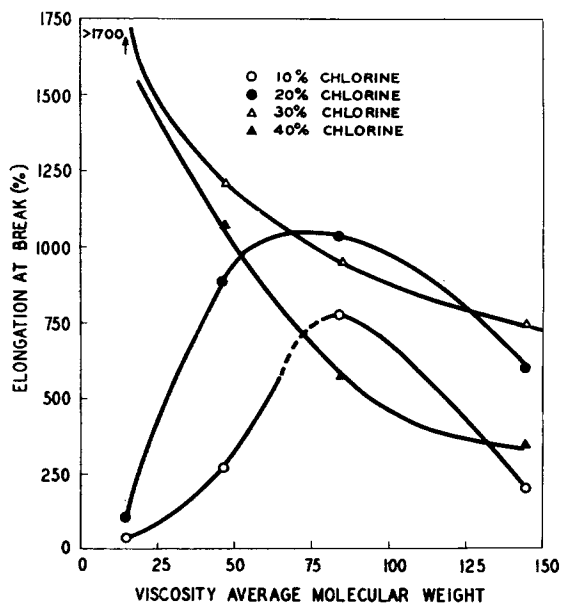


Fig. 9. Effect of  $\bar{M}_v$  on ultimate elongation of chlorinated linear polyethylene.

ishes. The higher the molecular weight, the higher the zero strength temperature.

Another property dependent chiefly on molecular weight is the elongation-at-break of the chlorinated polymers. Figure 9 shows the elongation-at-break of a series of chlorinated linear polyethylenes of increasing molecular weight. Noteworthy is the fact that, at chlorine contents of more than 30 wt.-%, the elongation is dependent only on molecular weight. However, below 30 wt.-% Cl, where the polymers are still partly crystalline, the crystallites behave as crosslinks to give low elongation with the low molecular weight polymers. Then as the molecular weight increases, the elongation increases and passes through a maximum, and then decreases once more at very high molecular weights.

### Random- vs. Block-Chlorinated Polymers

Chlorination of low-density polyethylene in solution results in a polymer in which the chlorine is substituted at random along the polymer chain.<sup>21</sup> Oaks and Richards<sup>15</sup> found that chlorination of low-density polyethylene in a partially crystalline condition yields a polymer with alternately non-chlorinated and highly chlorinated chain seg-

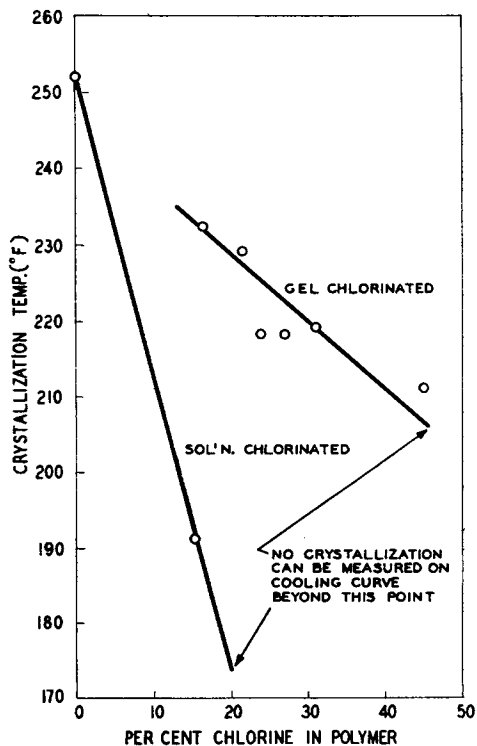


Fig. 10. Crystalline freezing point of chlorinated linear polyethylene.

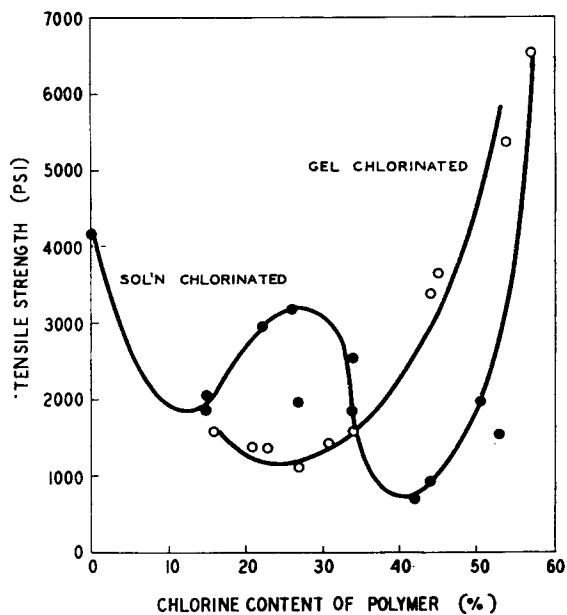


Fig. 11. Tensile strength of chlorinated polymer.

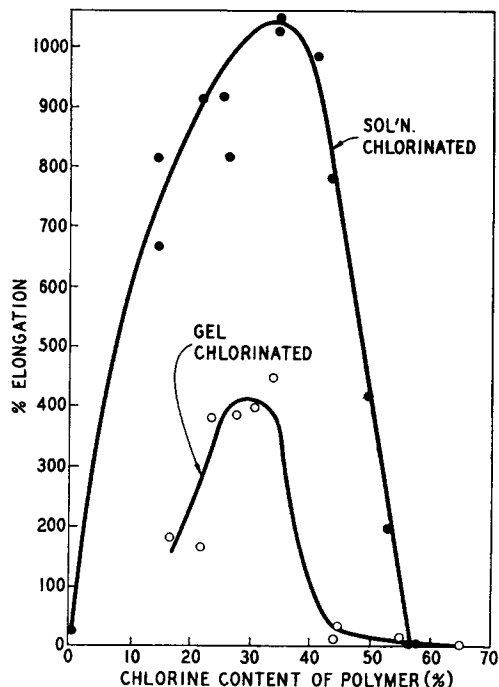


Fig. 13. Elongation of chlorinated polyethylene.

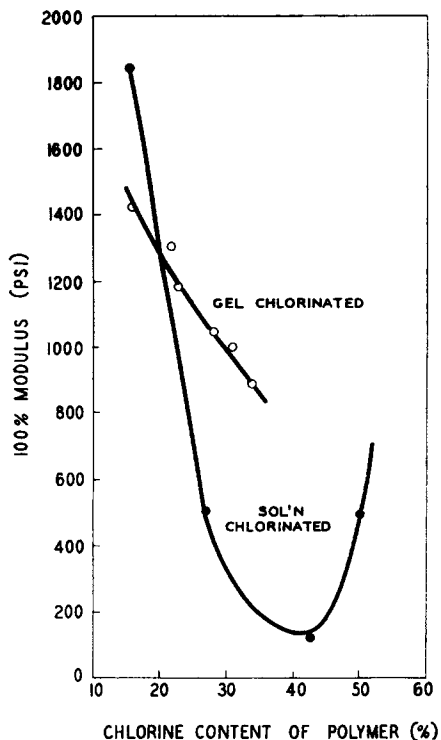


Fig. 12. 100% modulus of chlorinated polymer.

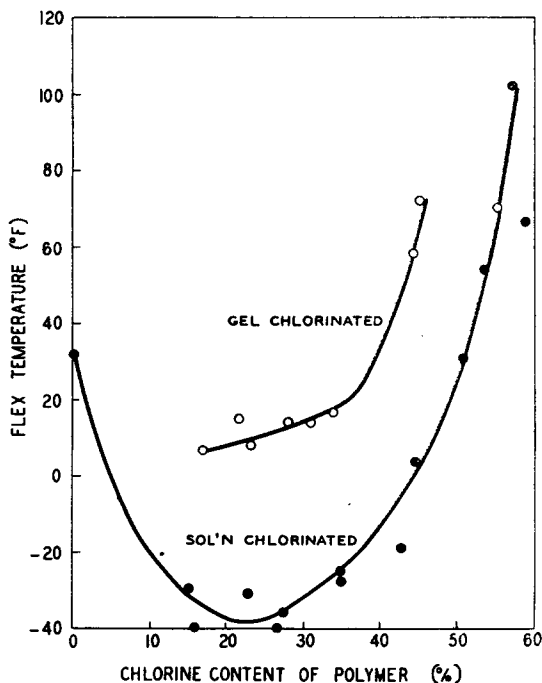


Fig. 14. Flex temperature of gel and solution chlorinated marlex polyethylene.

ments. This was accomplished by chlorinating polyethylene swollen by carbon tetrachloride. However, high-density polyethylene cannot be chlorinated in the swollen, partly crystalline state in the same manner as the low-density poly-

ethylene. It is more crystalline and does not swell to any practical extent, but rather has a sharp solution point.

In order to obtain chlorinated high-density polyethylene with blocks of chlorinated and rela-

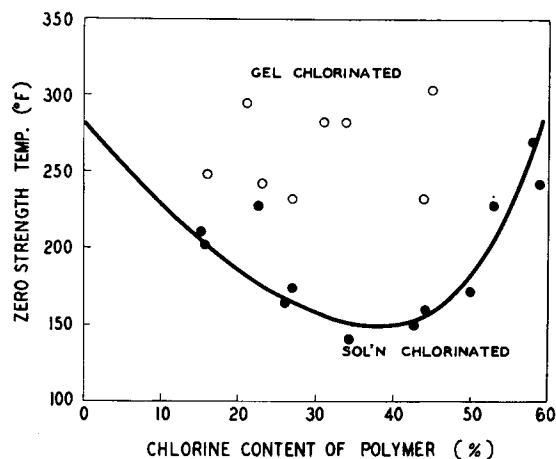


Fig. 15. Zero strength temperature of gel and solution chlorinated linear polyethylene.

tively unchlorinated segments, the polyethylene was first chlorinated as a solution to destroy some of the crystallinity. The solution was then cooled, and the polymer allowed to crystallize as a gel or slurry. This gel was then chlorinated further. The properties of the products were compared with those obtained by chlorination entirely in solution.

That the block-chlorinated materials retain some crystallinity at higher chlorine contents may be seen in Figure 10, where crystalline freeze points of the two types of chlorinated polymers are shown. The crystalline freeze point of the solution-chlorinated polymer disappears at chlorine contents

slightly above 15 wt.-% while that of the block-chlorinated polymer disappears at above 4 wt.-% Cl.

The properties of the block-chlorinated polyethylene reflect the presence of crystallinity. The tensile strength of the block-chlorinated products are lower than for the solution-chlorinated polymers below 35 wt.-% Cl (Fig. 11). The crystallites prevent the chains from orienting rapidly enough, under the stress applied to obtain the reinforcement from orientation exhibited by those of the solution-chlorinated products. Above about 35 wt.-% Cl content, the gel-chlorinated products have the higher tensile strength. The 100% modulus is much higher for the block-chlorinated polymer (Fig. 12), and the elongation lower (Fig. 13). The flex temperature is higher for the block-chlorinated polyethylene (Fig. 14). The zero-strength temperature of the products obtained from the two types of chlorination is shown in Figure 15. The values are higher for the block-chlorinated polymer.

Variation in chlorination conditions produces polymers containing the same amount of chlorine but possessing widely different physical properties.

#### Comparison of Properties of Flexible Chlorinated Polyethylene with Plasticized Polyvinyl Chloride

High-density polyethylene chlorinated in solution to a chlorine content between 15 and 35 wt.-% is a new flexible thermoplastic polymer. The prop-

TABLE II  
General Physical Properties of Chlorinated Linear Polyethylene and Polyvinyl Chloride\* (PVC)

	Chlorinated polyethylene (25% chlorine)				Polyvinyl chloride			
	1KC		1MC		1KC		1MC	
	K	Dx	K	Dx	K	Dx	K	Dx
Density	1.062				1.259			
Moldability	Good				Good			
Hardness, Shore D	25				35			
Impact strength, ft.-lb.	Too flexible				Too flexible			
Tensile strength, p.s.i.	2000-2400				2710			
Elongation, %	1600-1800				340			
100% Modulus, p.s.i.	400				1428			
Zero strength temp., °F.	160				247			
Refractive index	1.5194				1.544			
Brittleness temp., °F.	-153				32			
Flammability	Burns $\frac{4}{5}$ " min.				Self-extinguishing			
Flex temp., °F.	-30				-19			
Tensile impact strength, ft./in. <sup>2</sup>	405				340			
Heat distortion, °F.	10				32			
Dielectric constant (K) and Dissipation factor (Dx)	1KC		1MC		1KC		1MC	
	K	Dx	K	Dx	K	Dx	K	Dx
	6.13	0.0190	4.26	0.134	5.95	0.0113	3.38	0.0958

\* Containing 50 phr dioctylphthalate.

erties of this material at 25 wt.-% Cl were compared with the properties of plasticized polyvinyl chloride. A list of general physical properties are given in Table II. The chlorinated poly-

ethylene has good flexibility, tensile strength, and high elongation. It has a lower modulus and zero-strength temperature than the plasticized polyvinyl chloride. Its low temperature properties such as flex and brittleness temperature are superior.

TABLE III  
Film Properties of Chlorinated Linear Polyethylene and Plasticized Polyvinyl chloride

	Force direction*	Chlorinated polyethylene	Polyvinyl chloride
Tensile strength, p.s.i.	MD	3851	4930
	TD	3844	4680
Elongation, %	MD	855	240
	TD	855	240
Tear strength, g./mil	MD	942	210
	TD	856	201
Zero strength temp., °F.		170	215
Elmendorf tear strength, g./mil		266	—
Burst strength		Greater than 7 ft.	Greater than 7 ft.
Moisture vapor transmission, g./mil/100 in. <sup>2</sup> per 24 hr. at 90% relative humidity and 100°F.		7.8	7.23
Oxygen permeability, cc. × cm./sec./cm. <sup>2</sup> /cm. Hg		0.11 × 10 <sup>-9</sup>	0.10 × 10 <sup>-9</sup>

\* MD, machine direction; TD, transverse direction.

TABLE IV  
Properties of Filled Chlorinated Linear Polyethylene, with and without Plasticizer and Polyvinyl Chloride Plasticized with 50 phr Dioctyl Phthalate (Titanium Dioxide Filler)

Ti-O <sub>2</sub> -phr	Tensile, p.s.i.		Elongation, %		100% Modulus, p.s.i.		Flex temp., °F.	
	Cl PE	PVC	Cl PE	PVC	Cl PE	PVC	Cl PE	PVC
0	2000	2340	1275	116	—	—	—43	—
10	1718	2357	1840	148	226	1170	-32	-33
20	1695	2640	1830	118	226	2510	-33	-20
30	1740	2350	1890	133	23	2220	-29	-20
40	1620	2010	1720	124	260	1880	-28	-13
50	1530	2040	1560	128	255	1780	-28	-23
100	1770	2270	1420	223	335	2120	-26	-23
150	900	2310	630	91	463	—	-23	—
200	968	2420	550	58	558	—	-16	-16
300	1216	2810	365	28	858	—	-15	-10
400	1537	996	18	5	—	—	-11	—

Chlorinated Linear Polyethylene with 50 phr DOP<sup>a</sup>

0	1230	1330	—	-76
100	1511	1188	162	-75
600	849	223	692	-48

<sup>a</sup> Diisobutylphthalate.

The properties of the films are shown in Table III. The elongation and tear strength are considerably higher than can be obtained with the polyvinyl chloride formulation. The moisture vapor transmission and oxygen permeability are comparable to the polyvinyl chloride film.

An interesting property of chlorinated polyethylene is its capacity for fillers. For example, Table IV shows that as much as 400 parts of titanium dioxide can be incorporated into chlorinated polyethylene. It will accept 300 parts of bentonite clay, and such other fillers as carbon black. A plasticizer such as dioctyl phthalate will allow even higher loadings.

### Vulcanized Chlorinated Polyethylene

A brief study of vulcanized, chlorinated high-density polyethylene was made. In blends with pale crêpe or Philprene 1500 in white sidewall compounds, the vulcanizates all showed good ozone resistance. The gum stock was quite soft while hot but became hard on cooling. These results (Table V) indicate that with a suitable compounding recipe good ozone-resistant stocks may be formulated with chlorinated linear polyethylene.

TABLE V  
Vulcanized Chlorinated Polyethylene Stocks<sup>a</sup>

	100	50	50
Chlorinated polyethylene (25% Cl)	100	50	50
Pale crêpe	—	50	—
Philprene 1500 <sup>b</sup>	—	—	50
TiO <sub>2</sub>	—	50	50
Compression set	23.2	13.9	10.7
At 80°F.:			
300% Modulus, p.s.i.	780	320	525
Tensile, p.s.i.	1650	1800	1275
Elongation, %	430	650	460
200°F. Tensile, p.s.i.	200	100	200
ΔT, °F.	(°)	43.9	60.8
Resilience	72.4	79.7	72.5
Flex life (M)	0.4	16.4	0.7
Shore hardness, A	70.5	58	66.5
Ozone resistance <sup>d</sup>	0	0	0
Gehman freeze point, °C.	-30	-42	-41

<sup>a</sup> Sulfur cure: 307°F. for 1/2 hr.

<sup>b</sup> SBR type of rubber.

<sup>c</sup> Crumbled.

<sup>d</sup> Relative rating after 14 days: 0, no cracks; 10, many large cracks.



### Chlorosulfonated Polymers

Chlorosulfonated ethylene polymers are already of commercial importance as elastomers. They are marketed by Du Pont under the trade name of Hypalon. In this study, other chlorosulfonated ethylene polymers and copolymers were compounded, cured, and tested as elastomers. The compounding formulation used in the crosslinking of the experimental polymers is a recipe recommended for Hypalon polymers (Table VI) and is undoubtedly not the optimal curing system for all the experimental polymers. However, it should serve for the purpose of a general evaluation of the chlorosulfonated polymers.

TABLE VI  
Compounding Formulation and Curing Equations

Recipe	Parts
Chlorosulfonated polymer	100
Purecal S.C.	80
Ex. It. calcined MgO	20
Staybelite resin	2.5
Tetrone A	1.0
$4\text{RCOOH} + 2\text{MgO} \rightarrow 2(\text{RCOO})_2\text{Mg} + 2\text{H}_2\text{O}$	
1. $2\text{RSO}_2\text{Cl} + 2\text{H}_2\text{O} \rightarrow 2\text{HCl} + 2\text{RSO}_2\text{OH}$	
2. $\text{MgO} + 2\text{HCl} \rightarrow \text{H}_2\text{O} + \text{MgCl}_2$	
3. $\text{MgO} + 2\text{RSO}_2\text{OH} \rightarrow \text{H}_2\text{O} + (\text{RSO}_2\text{O})_2\text{Mg}$	
$2\text{RSO}_2\text{Cl} + 2\text{MgO} \rightarrow \text{MgCl}_2 + (\text{RSO}_2\text{O})_2\text{Mg}$	

First, a study was made on the effect of degree of chlorination on physical properties. A 93/7 low-pressure ethylene/propylene copolymer was used in this study. The best balance of rubbery properties was obtained on a polymer containing about 30% Cl and  $1.4 \pm 0.3\%$  sulfonyl type of sulfur. This agrees with published data on

chlorosulfonated high-pressure polyethylene. Properties of these polymers are summarized in Table VII. Over the range of chlorine and sulfur content investigated, tensile strength varied between about 2850 and 3400 p.s.i. and hot tensile strength (200°F.) varied between 1300 and 2100 p.s.i. It appears then that degree of chlorination has little effect on the tensile properties of these polymers once they are crosslinked. Tensile properties seem to be a function of the base polymer. The elongation was optimum at about 30–33% Cl and decreased as the chlorine content was increased. The residual elongation was found to be poor, possibly as a result of orientation of these chlorinated linear polymers. The resilience decreased with increasing chlorine content with polymers of about 30% Cl showing good resilience. The heat build-up varied between about 50 and 70°F. at the chlorine and sulfur level studied. The Gehman freeze point increased with increasing chlorine content. At 30% it was about  $-25^\circ\text{C}$ .

The base polymer was then varied to determine this effect on the physical properties of the chlorosulfonated products. The results are summarized in Table VIII. The two copolymers gave the best physical properties. Elongation-at-break, resilience, and flex life were superior to the high-density homopolymer. All the products from linear ethylene polymers and copolymers were superior to products from the low-density polyethylene in tensile strength, elongation, 200°F. tensile strength, resilience, and flex life. All the chlorosulfonated polymers, except polypropylene, were similar in Gehman freeze point; heat build-up varied from 50 to 65°F. The products from the linear polymers showed higher residual elongation. Hypalon-20 showed no permanent set in this experiment.

TABLE VII  
Properties of Chlorosulfonated<sup>a</sup> Ethylene/Propylene Copolymers of Variable Chlorine Content

Chlorine, %	Tensile, p.s.i.	Hot tensile, %	Elongation, %	Residual elongation, %	Resilience, %	Heat build-up $\Delta T$ , °F.	Gehman freeze point, °C.
29	3200	2000	350	25	70	63	-23
30	2900	1300	325	20	64	58	-25
33	2850	1850	400	12	69	62	-16
34	3400	1700	325	20	65	55	-17
36	3100	—	400	10	57	63	-13
37	3300	2100	325	9	54	—	-12
42	2850	1700	300	5	—	68	-13
46	3150	2000	250	7	55	52	-13
High pressure Polyethylene control (Hypalon-20)							
29	2300	1000	225	0	63	65	-22

A chlorosulfonated polypropylene gave a hard stock with a high Gehman freeze point.

The effect of molecular weight, as measured by melt index, on the properties of chlorosulfonated

polymers was studied by using ethylene/1-butene copolymers containing from 4.1 to 5.5% combined 1-butene. A range of melt indices from 0.5 to 18 was examined. Table IX lists the results. Ten-

TABLE VIII  
Variable Base Polymers (Cl 29%)

Base polymer	Melt index	Sulfur, %	Tensile, p.s.i.	Elongation, %	Residual elongation, %	200-°F., Tensile, p.s.i.	$\Delta T$ , °F.	Resilience, %	Flex life, <i>M</i>	Gehman freeze °C.
Et/Pr, 93/7	0.9	1.59	3200	350	25	2000	63	70	(30%) <sup>a</sup>	-23
Et/Bu-1, 96/4	2.3 HLM <sup>b</sup>	1.32	3600	350	30	2000	50	69	30	-19
Et/Bu-1, 96/4	2.3 HLM <sup>b</sup>	1.86	3600	200	24	1800	Too hard	68	6	-18
Linear polyethylene	0.9	1.85	3200	200	10	1700	—	65	—	-19
Linear polyethylene	0.9	0.94	2100	240	44	900	—	65	—	-22
Polypropylene		1.95	3400	110	3	1500	Too hard	Too hard	22.5% <sup>a</sup>	ca. +20
DYNH		1.97	3200	200	11	1500	—	—	—	-26
Hypalon		1.74	2500	225	3	1250	55	62	<0.1	-22
Hypalon-20		1.12	2300	225	0	1000	65	63	<0.1	-22

<sup>a</sup> Broken at 50,000 flexures.

<sup>b</sup> HLM: high load melt index (10 × standard weight)

TABLE IX  
Variable Melt Index Et/1-Bu Copolymers  
(1-Bu, 4.1-5.5)

Base polymer melt index	Cl, %	S, %	Raw ML-4	Tensile, p.s.i.	Elongation, %	Residual elongation, %	$\Delta T$ , °F.	Resilience, %	Gehman freeze, °C.	Extrusion ratings
0.510	35.7	1.7	59	2875	310	39	52.1	60.6	-23	5-
0.946	35.9	1.7	82	3225	290	7	55.8	46.9	-18	7-
1.024	34.1	1.5	57	3075	270	12	61.2	56.4	-20	7+
5.021	33.4	1.5	43	2875	210	7	58.8	52.0	-19	9
13.550	35.3	1.6	33	3025	200	5	60.5	47.0	-18	10+
18.308	33.5	2.1	27	3000	205	4	57.8	57.4	-13	11-
Hypalon-20	29.4	1.1	50	2300	200	1	63.8	62.8	-18	11-

TABLE X  
Effect of Comonomer Ratios on Chlorosulfonated Copolymer (Et/1-Bu)

1-Bu-tene, %	Melt index	Cl, %	S, %	Raw ML-4	Tensile, p.s.i.	Elongation, %	Residual elongation, %	$\Delta T$ , °F.	Resilience, %	Gehman freeze, °C.	Brittle points, °F.	Extrusion ratings
0	21.5	30.7	1.37	19	2450	265	33	62.8	66.3	-16	-50	9-
4.5	17.6	30.5	1.45	21	2150	320	31	65.9	61.1	-17	-37	10+
7.6	14.1	29.6	1.6	23	2500	310	23	61.5	63.9	-17	-43	10-
10.5	16.7	30.5	1.58	18	2275	310	24	61.5	62.1	-16	-45	11
Alathon-10	2.1	30.0	1.3	40	2400	330	23	65.5	63.4	-23	-45	9-
Hypalon-20	—	29.4	1.12	30	2200	260	8	62.5	61.5	-22	-52	7+

sile strength, resilience, and Gehman freeze point varied over a narrow range with melt index. The two properties which are improved by going to higher melt index (lower molecular weight) are residual elongation and processability.

To study the effect of the number of side groups on the base polymer on the properties of the chlorosulfonated products, a series of ethylene polymers of low molecular weight containing from 0 to 10% combined 1-butene were evaluated. The results are presented in Table X. It appears that the addition of ethyl side groups up to 10% has little effect on the physical properties of the vulcanizates. The copolymers still show a high residual elongation. On the basis of polymer chain structure it is difficult to explain, with our data, the low residual elongation of Hypalon, since the vulcanizate from chlorosulfonated Alathon-10, a branched polyethylene, gave high residual elongation.

#### SUMMARY AND CONCLUSIONS

The properties of chlorinated and chlorosulfonated polymers and copolymers of ethylene have been investigated.

**Chlorinated Polymers.** The properties of chlorinated polyolefins are affected by degree of chlorination, structure of the polymer chain, molecular weight, and chlorination conditions. As the amount of chlorine substitution in the polymer is increased, there is obtained a family of thermoplastics which change progressively in properties, from semirigid, to flexible, to rubbery, to hard and rigid plastics. A maximum in tensile strength exists in the flexible plastic region. This peak is a reflection of the semicrystalline nature of the polymer.

When the structure of the basic hydrocarbon polymer chain is altered by introduction of side chains, then, on chlorination, the maximum in tensile strength is shifted to lower chlorine contents. In highly branched polymers, such as high-pressure polyethylene, this maximum disappears altogether.

Increasing the molecular weight of the ethylene polymer gives rise to products of higher tensile strength, higher zero-strength temperature, and lower elongation. The flex temperature is increased slightly.

In addition to basic olefin polymer differences, entirely different physical properties can be obtained by changing the chlorination conditions. Comparison of block-chlorinated polyethylene with

solution-chlorinated polyethylene shows that the block-chlorinated polymer retains crystalline regions up to 40 wt.-% Cl. Consequently, the block-chlorinated polymer has higher modulus, lower elongation, higher flex temperature, and higher zero-strength temperature.

Chlorinated linear polyethylene of 15-35 wt.-% Cl is a new flexible plastic. Compared with plasticized polyvinyl chloride, it has good flexibility, tensile strength, and high elongation. Its low-temperature properties such as flex and brittleness temperature are superior to polyvinyl chloride. It has a lower zero-strength temperature and lower 100% modulus. Its processing characteristics are good, and it can be loaded with large quantities of fillers. When vulcanized, the cured stocks are hard and have a high residual elongation. However, when blended with natural rubber, good ozone-resistant stocks are obtained.

**Chlorosulfonated Polymers.** Chlorosulfonated linear ethylene polymers and copolymer were tested as elastomers. The best balance of rubbery properties was obtained with polymer containing about 30 wt.-% Cl and  $1.4 \pm 0.3$  wt.-% sulfonyl type of sulfur. Stress-strain properties of the chlorosulfonated linear copolymers were better than those of the chlorosulfonated linear polyethylene or branched polyethylene. Poor residual elongation was characteristic of the chlorosulfonated linear polymers. An increase in the number of side groups in the basic polymer chain did not affect residual elongation.

The authors gratefully acknowledge the assistance and advice received from many associates in the Plastics, Rubber, and Physics Branches of the Research Division of Phillips Petroleum Company.

#### References

1. Dow Chemical Company, Belg. Pat. 552,158.
2. Dynamit, A.-G., Belg. Pat. 581,319.
3. Ernsberger, M. L., U. S. Pat. 2,503,252 (April 11, 1950), assigned to E. I. du Pont de Nemours & Company.
4. Farbenfabriken Bayer A.-G., Brit. Pat. 773,922 (May 1, 1957); 705,974 (March 14, 1954); 709,963 (June 2, 1954).
5. Farbwerke Hoechst A.-G., Belg. Pat. 578,595.
6. Fawcett, E. W., Brit. Pat. 481,515 (March 11, 1938).
7. Heitzer, E., A. G. M Gumboldt, and G Messwab, U. S. Pat. 2,906,743, assigned to Farbwerke Hoechst A.-G.
8. Hoerner, F. D., and H. W. Smeal, U. S. Patent 2,913,449 (November 17, 1949), assigned to Dow Chemical Company.
9. McAlevy, A., Can. Pat. 533,017 (November 13, 1956); U. S. Pat. 2,405,971 (August 20, 1946), assigned to E. I. du Pont de Nemours & Company.
10. Montecatini Belg. Pat. 540,362; 576,340

11. Myles, J. R., P. J. Garner, and Imperial Chemical Industries, Ltd., Brit. 575,096 (February 4, 1946).
12. Myles, J. R., L. Snowden, and Imperial Chemical Industries, Ltd., Brit. Pat. 574,941 (January 20, 1946).
13. Myles, J. R., and S. B. J. Stephen, U. S. Pat. 2,398,803 (April 23, 1946), assigned to Imperial Chemical Industries, Ltd.
14. Noeske, H., U. S. Pat. 2,928,819 (March 15, 1960), assigned to Ruhrchemie A.-G.
15. Oaks, W. G., and R. B. Richards, *Trans. Faraday Soc.*, **42A**, 197 (1946).
16. Petrochemicals Limited, Belg. Pat. 548,099.
17. Renfrew, A., and P. Morgan, *Polythene*, Interscience New York (1957), pp. 267-272.
18. Ruhrchemie A. G., Belg. Pats. 593,466; 545,364.
19. Schildknecht, C. S., *Vinyl and Related Polymers*, Wiley, New York, 1952, p. 527.
20. Solvay et Cie, Belg. Pat. 561,764.
21. Thompson, H. W., and P. Torkington, *Proc. Royal Soc.*, **184A**, 21 (1945); *Trans. Faraday Soc.*, **41**, 246 (1945).

### Synopsis

The properties of chlorinated and chlorosulfonated ethylene polymers and copolymers have been examined. The effect of such variables as polymer chain structure, molecular weight, degree of chlorination, and chlorination conditions was studied. A variation in physical properties of different polyolefins chlorinated to the same degree is attributed to differences in residual crystallinity in the chlorinated product. Chlorinated linear polyethylenes are more crystalline than chlorinated branched polyethylene and are semicrystalline, flexible plastics in the 15-35 wt. % range. The chlorinated branched polyethylenes of this chlorine content are soft and rubbery. Chlorination conditions can influence the degree of residual crystallinity in the chlorinated product, and hence have a pronounced effect on the properties of the products. Molecular weight of the polymer and degree of chlorination influence the properties of the chlorinated product. Chlorosulfonated linear ethylene polymers and copolymers were tested as elastomers. Stress-strain properties were better for the chlorosulfonated linear copolymers as compared to chlorosulfonated linear polyethylene or branched polyethylene. Poor residual elongation was characteristic of the chlorosulfonated linear polymers. An increase in the number of side groups in the basic polymer chain did not affect residual elongation.

### Résumé

Les propriétés des polymères et copolymères chlorés et chlorosulfonés d'éthylène ont été examinées. L'effet des variables telles que la structure de la chaîne du polymère, le poids moléculaire, le degré de chloration et les conditions de chloration, a été étudié. Une variation dans les propriétés

physiques des différentes polyoléfines chlorées jusqu'à un même degré est attribuée aux différences dans la cristallinité résiduelle du produit chloré. Des polyéthylènes linéaires chlorés sont plus cristallins que le polyéthylène ramifié chloré; ils sont des plastiques semi-cristallins et flexibles, le domaine des teneurs en chlore allant de 15 à 35%. Les polyéthylènes branchés de cette composition en chlore sont doux et caoutchouteux. Les conditions de chloration peuvent influencer le degré de la cristallinité résiduelle dans le produit chloré et, dès lors, elles ont un effet prononcé sur ces propriétés-la. Le poids moléculaire du polymère et le degré de chloration influencent les propriétés du produit chloré. Des polymères et copolymères d'éthylène linéaires chlorosulfonés ont été testés comme des élastomères. Les propriétés de force de tension étaient meilleures pour les copolymères linéaires chlorosulfonés que pour le polyéthylène linéaire chlorosulfoné ou le polyéthylène ramifié. Une faible élongation résiduelle était caractéristique pour les polymères linéaires chlorosulfonés. Une augmentation dans le nombre des groupes latéraux dans la chaîne du polymère de base n'affecte pas l'élongation résiduelle.

### Zusammenfassung

Es wurden die Eigenschaften von chlorierten und sulfochlorierten Äthylenpolymeren und -copolymeren untersucht. Der Einfluss einiger Variabler, wie Kettenstruktur der Polymeren, Molekulargewicht, Chlorierungsgrad und Chlorierungsbedingungen wurden untersucht. Unterschiede in den physikalischen Eigenschaften verschiedener Polyolefine mit gleichem Chlorierungsgrad werden den Unterschieden in der Restkristallinität des chlorierten Produkts zugeschrieben. Chlorierte lineare Polyäthylene sind kristalliner als chlorierte verzweigte Polyäthylene; sie bilden innerhalb eines Chlorgehalts von 15 bis 35 Gewichtsprozenten halbkristalline, flexible plastische Stoffe. Chlorierte verzweigte Polyäthylene mit diesem Chlorgehalt sind weich und gummiartig. Die Chlorierungsbedingungen können das Ausmass der Restkristallinität im chlorierten Produkt beeinflussen und üben daher einen starken Effekt auf die Eigenschaften der Produkte aus. Molekulargewicht des Polymeren und Chlorierungsgrad beeinflussen die Eigenschaften des chlorierten Produkts. Sulfochlorierte lineare Äthylenpolymere und -copolymere werden in Hinblick auf ihre Verwendbarkeit als Elastomere getestet. Das Spannungs-Dehnungsverhalten der sulfochlorierten linearen Copolymeren war besser als das der sulfochlorierten linearen oder verzweigten Polyäthylene. Geringe bleibende Dehnung war für die sulfochlorierten linearen Polymeren charakteristisch. Ein Ansteigen der Zahl der Seitengruppen in der zugrundeliegenden Polymerkette beeinflusst die bleibende Dehnung nicht.

Received February 9, 1961