

CHLOROSULFONATED POLYETHYLENE

Chlorosulfonated polyethylene, CSM, [68037-39-8], as described according to ASTM D1418, represents a family of cureable polymers, ranging from soft and elastomeric to hard and plastic, containing pendent chlorine and sulfonyl chloride groups. Chlorosulfonated base resins, other than polyethylene, are closely related and are therefore considered a part of this family. Addition of chlorine and sulfonyl chloride groups onto these base resins enhances solubility in common solvents and, when properly compounded and cured, gives resistance to light discoloration, oil, flame, and oxidizing chemicals. Resistance to thermal degradation and ozone attack result from the absence of unsaturation in the polymer backbone. The additional functionality of comonomers and grafts contribute to adhesion and polymer mechanical reinforcement. This combination of value-added properties promotes special end use applications in coatings, adhesives, roofing membranes, electrical wiring insulation, automotive and industrial hose, tubing and belts, and in molded goods.

In the 1940s, Du Pont chemists began a study of chlorinated low density (branched) polyethylene, in response to wartime needs for new synthetic rubbers. The initial result was a rubbery product at about 30% chlorine, called S-1, with vulcanizates having good oil, chemical, and heat resistance properties (1–3). Vulcanization could only be accomplished with peroxides (4), however, which greatly limited its service. Subsequently, simultaneous chlorination and chlorosulfonation of these resins produced polymers with a sulfonyl chloride cure site which allowed cross-linking with safe curatives known in the industry (5). This product, with a molecular weight of about 20,000, was initially called S-2, but was later commercialized in 1952 as Hypalon 20. It was followed in 1957 by commercialization of a lower molecular-weight version called Hypalon 30, targeted for solution applications.

Linear polyethylene (high density) was introduced in the late 1950s, with the development of coordination catalysts. Chlorosulfonation of these base resins gave products that were superior to the earlier, low density types in both chemical resistance and mechanical properties and with distinct advantages in rubber processibility (6, 7).

Introduction of linear low density polyethylene in the 1970s and 1980s offered yet another design parameter, giving chlorosulfonated products with the advantages of linear types but with improved low temperature performance (8).

Extension of the chlorosulfonation technology to base resins other than polyethylene, where value can be added, seems a logical next step. Polypropylene and ethylene copolymers containing additional functionality, ie, maleic anhydride graft, vinyl acetate, acrylic acid, etc, have been chlorinated and chlorosulfonated to broaden the application base, particularly in coatings and adhesives (9, 10).

The combined worldwide market for this entire family of elastomers had grown to about 48,000 metric tons per year in 1991.

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Table 1. Effect of Chlorine Content of CSM on Crystallinity and T_g ^a

Chlorine content, %	Linear ΔH , J/g ^b	T_g , °C	Branched ΔH , J/g ^b	T_g , °C
20	43	−43	9.2	−46
25	24	−26	2.5	−31
30	9	−13	0.2	−19
35	0.1	+4	0.0	+10
40	0.0	+9	0.0	+13
45	0.0	+19	0.0	+27
52			0.0	+65
64	0.0	+95		

^a Ref. 11.

^b Heat of fusion of the polymer. To convert J to cal, divide by 4.184.

1. Physical Properties

The rubbery character of the chlorosulfonated polyethylene is derived from the flexibility of the polyethylene chain in the absence of crystallinity. Introduction of chlorine onto the polymer chain provides sufficient molecular irregularity to prevent crystallinity in the relaxed state, but glass-transition temperature, T_g , increases with chlorine content. The degree of rubberiness is, therefore, a function of the balance of residual crystallinity and T_g . The optimum chlorine content for most general rubber applications is the minimum amount required to completely destroy the crystallinity. This chlorine amount varies with the amount of crystallinity in the starting resin. As the chlorine content increases beyond this optimum level, the glass-transition temperature becomes more dominating and the polymers become more plastic and eventually hard and brittle (Table 1).

These values assume chlorination in carbon tetrachloride solution under homogeneous conditions favoring random distribution of chlorine atoms along the chain. Viscous reaction conditions, faster chlorine addition rates, lower temperature conditions, etc, can lead to higher ΔH at equivalent chlorine levels because of more blocky chlorine distribution on the polymer chain.

The sulfonyl chloride groups provide cross-linking sites for nonperoxide curing procedures. Although concentrations as high as 4–5% for specific applications may be achieved, the optimum level for most general rubber applications is normally about 1–1.5 wt %, measured as sulfur, or one sulfonyl chloride group for every 85–110 carbon atoms on the chain. The sulfonyl chloride group, because of its bulk, is more responsible for interference in crystallinity than chlorine atoms on an equimolar basis, but is less important because of its low level.

CSM products may be divided into three groups depending on the type of precursor resin: low density (LDPE), high density (HDPE), and linear low density (LLDPE). LDPE is made by a high pressure free-radical process, while HDPE and LLDPE are made via low pressure, metal coordination catalyst processes (12) (see Olefin polymers).

The uncured physical properties of polymers within each group depend on the molecular weight, molecular-weight distribution, and the extent and distribution of chlorination and chlorosulfonation. The molecular weight, molecular-weight distribution (MWD), and chain branching are generally set by the choice of parent polyethylene resin, ie, neither chain scission nor cross-linking take place during chlorosulfonation. This is illustrated by a comparison of gel-permeation chromatography (gpc) data of unchlorinated and chlorinated high density polyethylene, which show nearly identical molecular-weight distribution shape functions differing only in the chlorine content (Table 2) (13). The agreement of measured inherent viscosity values and those calculated from gpc indicate no significant long-chain branching in either the unchlorinated or chlorinated polymer.

Table 2. Comparison^a of Mol Wt Properties of HDPE and Chlorinated HDPE Chlorosulfonated Product

Properties	Polyethylene	Chlorinated ^b product
melt index ^c , g/10 min	5.6	
M_n	23,000	36,800
M_w	78,000	117,293
η_{inh}^d , dL/g (calc)	1.18	1.48
η_{inh}^d , dL/g (meas)	1.16	1.50

^a Gpc data.^b 35% Cl.^c Amount of polymer flowing through a std capillary viscosimeter 2.095-mm dia and 8-mm long at 190°C and a load of 2.16 kg for 10 min.^d Inherent viscosity = $\frac{\ln \eta_r}{c}$.**Table 3. Properties of Uncured CSM^a**

Property	CSM	HDPE	CSM	LLDPE	CSM	LDPE
Cl, wt %	21.5	27.7	22	30	20.8	29
sulfur, wt %	1.7	0.51	1.0	0.98	1.3	1.5
tensile strength, MPa ^b	13.4	10.9	9.3	12.9	5.4	0.48
elongation at break, %	420	880	1259	1935	2100	25
ΔH^c , J/g ^d	38	14	12	1.5	11	2

^a Ref. 14.^b To convert MPa to psi, multiply by 145.^c Heat of fusion.^d To convert J to cal, divide by 4.184.

These conclusions are further supported by expected physical properties of dried film of chlorosulfonated polyethylene from the different types of polyethylene (Table 3).

These values are given for polymers of narrow molecular-weight distribution, with number-average molecular weights (M_n) of about 20,000 prior to chlorination. Chlorination reactions are carried out under homogeneous conditions in CCl_4 solutions at temperatures between 90 and 110°C with viscosities at about 5 Pa (50 P).

The uncured property most often used for CSM in dry applications is *Mooney viscosity*, a low shear bulk viscosity (ca 1.6 s^{-1}) determined at 100°C. Mooney viscosity is a rubber industry standard used to predict raw rubber and compound processibility, ie, mixing, extrusion, molding, etc.

The bulk viscosity control parameter for CSM, as with other elastomers, is molecular weight (M_w) and molecular-weight distribution (MWD). Mooney viscosity for CSM is determined by selection of the polyethylene precursor.

The *melt index (MI)* of polyethylene is also a low shear measurement used in the plastics industry to predict processibility and properties. Both MI and Mooney viscosity are related to zero shear viscosity and, therefore, the weight average molecular weight (M_w). Mooney viscosity is directly proportional to M_w , and MI is inversely proportional to M_w . For this reason, polyethylene MI is usually specified for prediction of the CSM Mooney viscosity. Melt index, however, is not always a good measure of M_w , because in most cases it is measured in the non-Newtonian region of the flow curve. The shape and slope in this region are strongly affected by the MWD of the resin. To correct for this, a second MI measurement of polyethylene at a higher shear rate is often measured. The slope of the curve between these points is a function of MWD and may be used, in conjunction with MI, to more accurately predict the CSM viscosity. Increasing the chlorine content of the polymer backbone also increases Mooney viscosity because of increased chain entanglement and intermolecular

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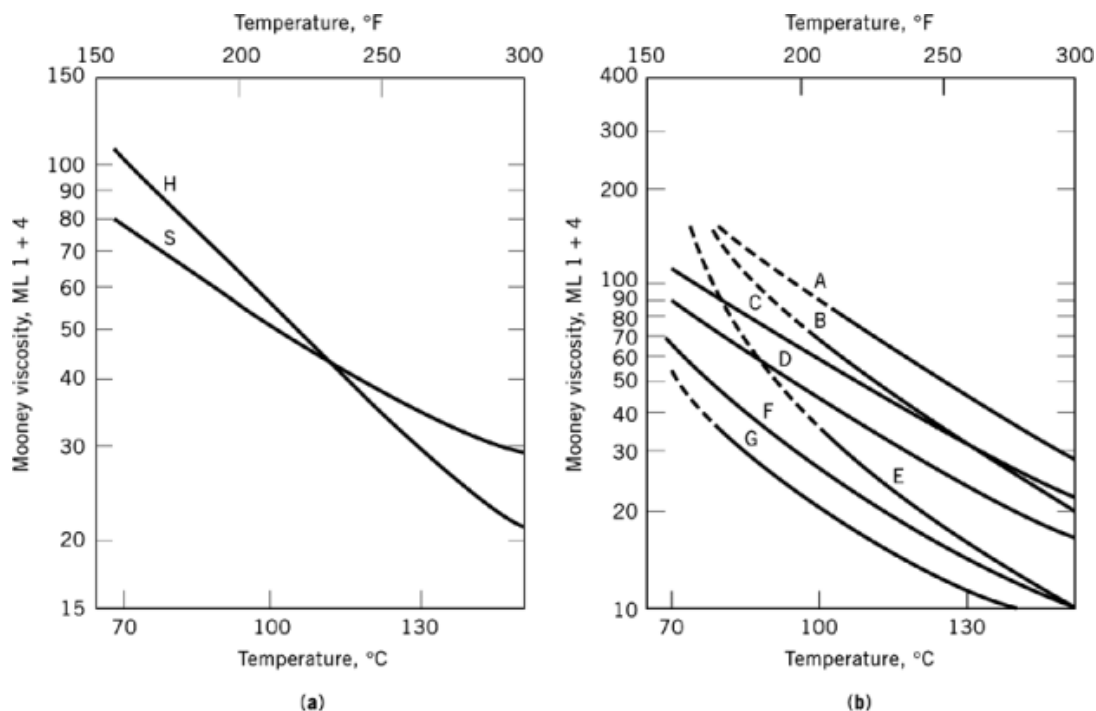


Fig. 1. Viscosity–temperature relationship of (a) Hypalon 40 (H) and SBR 1500 (S) and (b) various Hypalon polymers: A, Hypalon 4085; B, Hypalon 48; C, Hypalon 40; D, Hypalon 40S; E, Hypalon 45; F, LD999; and G, Hypalon 623.

hydrogen bonding. Generally the Mooney viscosity of the polymer doubles for each 10% chlorine increase at equivalent chain length.

Bulk viscosity for all elastomeric polymers decreases with increasing temperature. CSM viscosity decreases more rapidly with temperature than for most other elastomers because hydrogen bonding and increasing chain entanglement result in high apparent bulk viscosity at low temperatures. At higher temperatures, the hydrogen bonding disappears lowering the bulk viscosity. Figure 1 compares the temperature viscosity relationship of Hypalon 40 and SBR 1500, as well as the interrelationship of all CSM types (15). Among the various CSM types, the more rubbery grades are less temperature-sensitive than those whose chlorine levels place them outside this range because of the absence of crystallinity or glassy regions. The viscosity/shear rate relationship is as expected, ie, polymers with narrow MWD are less shear-sensitive than those with broad MWD (16).

2. Chemical Properties

The known chemistry of the functional groups in CSM, ie, chlorine and sulfonyl chloride groups, make reactions predictable from their functions in low molecular-weight substances. Acid, ester, and amide derivatives of the sulfonyl chloride group have been prepared and their infrared spectra have been studied (17). The chlorine content, at equivalent cross-link density and base resin type, is the principal factor in determining the chemical properties of the vulcanized CSM polymers. Figure 2 illustrates diagrammatically the general trends of several product properties with chlorine content. Actual values for these properties are not given because they depend

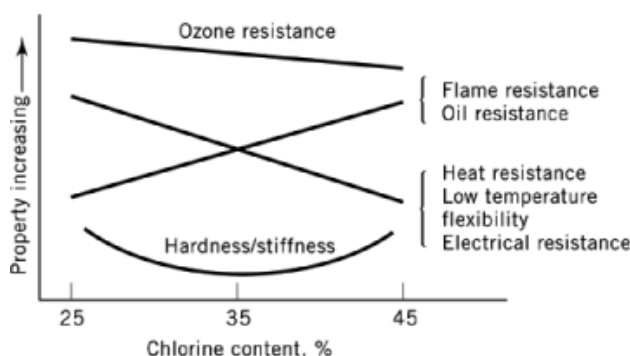


Fig. 2. Effect of varying chlorine content in CSM polymers.

Table 4. Chlorine Distribution in Chlorosulfonated Polyethylene

Structure type	% of Total chlorine	
	Branched PE	Linear PE
$\text{RCH}_2\text{—Cl}$	2.7	0.3
$\text{RCHCl—(CH}_2)_n\text{—CHCl—R}$ ($n > 2$)	71	83
($n < 2$)	18	11
RR'R''C—Cl	2–3.5	0.0
$\text{RCH}_2\text{SO}_2\text{Cl}$	0.08	0.0
$\text{R—CHCl—CH(SO}_2\text{Cl)—R}$	0.3	0.7
$\text{R—CH}_2\text{—CH(SO}_2\text{Cl)—CH}_2\text{—R}$	4.2	3.8

heavily on compounding, the curing system, and cure states. At low chlorine levels, the polymers retain some of the characteristics of the polyethylene. They are stiffer and harder because of residual polyethylene crystallinity. They also show good electrical properties, heat resistance, and low temperature flexibility compared to other CSM types. With increasing chlorine content, the polymers and vulcanizates become increasingly rubbery. The softest and most rubbery region is at the minimum chlorine level where the crystallinity disappears, which depends on the crystallinity of the original polyethylene. For branched polymers, ie, LDPE or LLDPE, at a density of 0.92, this chlorine level is about 30% or one chlorine atom for every seven carbon atoms. For HDPE, at 0.96 density, the optimum is about 35% or about one chlorine atom for every five carbon atoms. As the chlorine level is increased beyond this point, the polymers become stiffer again as the glass-transition temperature approaches ambient. These high chlorine types are characterized by excellent oil resistance, flame retardance, and solvent solubility, but have poor resilience and low temperature flexibility.

The distribution of chlorine atoms along the polymer chain has been studied in great detail. The distribution in various functional types is shown in Table 4 (18). High density polyethylene chlorosulfonated to 35% Cl and 1% S has been found to contain only 1.7% highly active chlorines, ie, reactive to weak bases. All of these are attributed to the chlorine in the sulfonyl chloride group and those in beta position to SO_2Cl . No vicinal chlorides groups were found (19).

Model studies with 1-chlorobutane and 1-chlorohexane show that further substitution is directed away from the chlorine substituent in decreasing intensity to four carbon atoms (20). However, the reaction conditions, solvent type, and chlorosulfonating agent can significantly affect the chlorine distribution. Thus CSM polymers prepared in carbon tetrachloride solution using chlorine and sulfur dioxide gas were found to match

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predictions for random substitution at 75°C (21), whereas a selective distribution was found when the reaction was carried out in chlorobenzene at its boiling point using sulfuryl chloride as the chlorosulfonating agent. Use of gaseous chlorine creates high local concentrations at the bubble interface in the reaction mass. A possible explanation is that the chlorination rate is faster than the diffusion rate, into the reaction mass, causing irregular distribution, resulting in blocky chlorine distribution and higher crystallinity. The melting point and heat of fusion of the polymer depend on the number and length of such blocks (22).

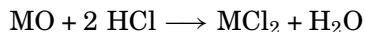
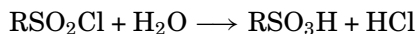
The sulfonyl chloride group is the cure site for CSM and determines the rate and state of cure along with the compound recipe. It is less stable than the Cl groups and therefore often determines the ceiling temperature for processing. The optimum level of sulfonyl chloride to provide a balance of cured properties and processibility is about 2 mol % or 1–1.5 wt % sulfur at 35% Cl. It also undergoes normal acid chloride reactions with amines, alcohols, etc, to make useful derivatives (17).

3. Vulcanization

Most end use applications of CSM, as with other thermoset polymers, involve mixing with various fillers, plasticizers, processing aids, curatives, etc, then shaping and cross-linking in its final form. Acid acceptors are required in CSM compounds because acidic by-products of curing reactions interfere with the cure and cause equipment corrosion. Acceptable acid acceptors include magnesia, litharge, organically bound lead oxide, calcium hydroxide, synthetic hydrotalcite, and epoxy resins. Zinc oxide or other zinc-containing process aids, ie, zinc stearate used for other elastomers, should be avoided because the zinc chloride formed during curing causes severe polymer degradation.

Compound formulations are chosen to accentuate desired end product properties, ie, heat resistance, water resistance, low temperature flex, or combinations of properties for specific applications, while maintaining cost goals (21). For some applications, ie, nuclear power cable, high filler loadings are undesirable because of their contribution to radiation leakage. Unlike most other elastomers, large quantities of reinforcing fillers are not required to achieve good mechanical properties for high density CSM vulcanizates (23). Carbon black fillers give the best reinforcement of physical properties and the best resistance to chemical degradation. Small amounts of carbon black can also give significant improvement in weatherability. Mineral fillers are used to take advantage of CSM's nondiscoloring characteristics. Clays, silicas, and calcium carbonate augment flame and heat resistance. White compounds include titanium dioxide for light stability. Plasticizers are added to reduce viscosity during processing and increase low temperature flexibility of the final product. Petroleum oils are widely used because of low cost. Ester plasticizers provide the best combination of low temperature flex, heat resistance, and mechanical property retention.

Early recommendations for cross-linking CSM involved the use of divalent metal oxides to form metal sulfonate cross-links (24). The mechanism involves the hydrolysis of the sulfonyl chloride group with a carboxylic acid, ie, stearic acid, which produces water at curing temperatures.



These cures, characterized by their ability to proceed at low temperatures, are accelerated by moisture and develop high modulus.

Three different covalent cure systems are commonly used: sulfur-based or sulfur donor, peroxide, and maleimide. These systems rely on a cross-linking agent and one or more accelerators to develop high cross-link density.

Sulfur-based cures give the widest flexibility in choice of compounding ingredients and are the most widely used. The cure involves the decomposition of sulfonyl chloride groups to form polymer radicals that react with active forms of activator decomposition products. The most common activators are dipentamethylenethiuram hexasulfide [971-15-3] (Tetrone A), tetramethylthiuram disulfide [137-26-8] (TMTD), and bisbenzothiazolyl disulfide [120-78-5] (MBTS). Litharge or a substitute is usually necessary to give high states of cure. The litharge probably reacts at cure temperature with the sulfur donor, eg, Tetrone A, to form dithiocarbamate and some active form of sulfur. The carbamate causes decomposition of the sulfonyl chloride group which then reacts with the activated sulfur to form a cross-link.

The best heat resistance is obtained when nickel dibutyldithiocarbamate [13927-77-0] (NBC) is incorporated into the compound. NBC contributes to the heat resistance by causing the elimination of unused sulfonyl chloride groups which are then unavailable for additional cross-linking during heat aging. The presence of large amounts of litharge probably also result in some ionic cross-link formation.

In the maleimide cure, the cross-linking agent is *N,N'*-*m*-phenylenedimaleimide [3006-93-7], HVA-2. This system has two significant advantages: litharge is not required for high cross-link density and low compression set may be obtained. The accelerators are weak bases, ie, *N,N'*-diphenylethylenediamine. The cure mechanism probably involves an amine-catalyzed decomposition of the sulfonyl chloride group or a path of radical anions. The cross-link probably involves the HVA-2. Calcium hydroxide or other SO₂ absorbers must be included for development of good mechanical properties.

Peroxide curing systems are generally the same for CSM as for other elastomers but large amounts of acid acceptor must be present to complete the cure. A small amount of a polyfunctional alcohol, ie, pentaerythritol (PER) in the compound significantly reduces the amount of base required by acting as a solubilizer. Triallyl cyanurate [101-37-1] is an additional cure promoter and leads to higher cross-link density.

A comparison of compound recipes and physical properties for the various cure systems is given in Table 5.

4. Uses

Commercial CSM polymers are currently made by E. I. du Pont de Nemours & Co., Inc. in Northern Ireland and the United States and by Toyo Soda Mfg. Ltd. in Japan. Commercial grades of CSM made by Du Pont under trade names Hypalon and Acsium are shown in Table 6. Similar grades are made by Toyo Soda under CSM TS and CSM CP trade names.

4.1. Solution-Grade Polymers

Hypalon 20 is made from a highly branched low density polyethylene (LDPE). It was the original Hypalon elastomer and was formerly used in the manufacture of molded and extruded goods. It was also used in premium-grade white sidewall tires for many years to resist ozone cracking. The base polyethylene contains about four lower alkyl branches and one long-chain alkyl branch for every 100 carbon atoms. This structure gives very rough extrudates unless heavily plasticized. At a chlorine content of 29%, it has slightly poorer oil resistance than CR. The branched-polymer structure, however, makes it readily soluble in common solvents and gives relatively low solution viscosity for its molecular weight. Thus it is useful in roof coatings and the manufacture of tarpaulins and colored awnings.

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Table 5. Comparison of CSM Cure Systems

Compound, phr	Sulfur cure	Maleimide	Optimum heat resistance	Peroxide
Hypalon 40	100	100	100	100
SRF Black	40	40	40	40
Litharge (PbO)	22		22	
Magnesia (MgO)	10	4	10	5
NBC	3		3	
Tetrone A			0.75	
benzthiazyl disulfide	0.5		0.5	
sulfur	0.56			
PER-200				3
calcium hydroxide		4		
<i>N,N'</i> - <i>m</i> -phenylethylenediamine		2	1	
HVA-2		3		
Varox powder				6
triallyl cyanurate				0.4
<i>Curing conditions</i>				
temperature, °C	153	153	153	160
time, min	30	30	30	20
<i>Vulcanizate properties</i>				
original modulus, 100%, MPa ^a	8.1	6.8	8.5	9.5
tensile strength, MPa ^a	27.5	23.1	31.4	27.6
elongation, %	245	300	285	320
compression set, %, 22 h at 70°C	30	19	23	13
<i>Heat-aged^b properties</i>				
tensile strength, MPa ^a	26.2	21.3	29.2	26.7
elongation, %	65	60	92	83
vol increase after 72 h at 100°C in ASTM #1 oil	12	14	5	7

^a To convert MPa to psi, multiply by 145.

^b After 7 days and 150°C

Table 6. Commercial CSM Grades

CSM grade	Chlorine content, %	Sulfur content, %	Mooney viscosity	Principal use
<i>From LDPE</i>				
Hypalons				
20	29	1.4	28	solutions
30	x43	1.3	30	solutions
<i>From HDPE</i>				
LD999	34	1.0	30	general-purpose
40S	35	1.0	45	general-purpose
40	35	1.0	56	general-purpose
4085	36	1.0	97	general-purpose
610	35	1.0	126	general-purpose
48	43	1.0	62	oil-resistant hose and freon hose
45	24	1.0	37	membranes
623	24	1.0	21	membranes
<i>From LLDPE^a</i>				
Acciums				
6367	26	1.0	40	auto belts
6932	30	1.0	60	auto belts
6983	26	1.0	90	auto belts and hose

^a Density = 0.92.

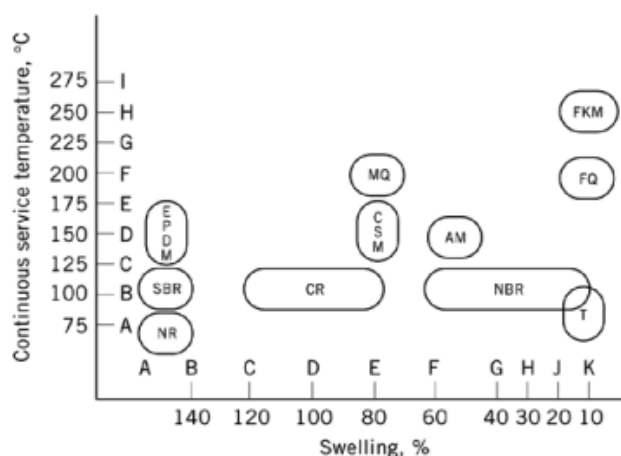


Fig. 3. Heat and oil resistance of CSM compared to other elastomers by ASTM D2000. A–K indicate grades of CSM. The other ASTM designations are as follows: AM, acrylic elastomers; CR, chloroprene rubber; EPDM, ethylene-propylene-diene rubber; FKM, fluorocarbon elastomers; FQ, fluorosilicones; MQ, silicone rubber; NBR, nitrile-butadiene rubber; NR, natural rubber; SBR, styrene-butadiene rubber; and T, thiokol rubber.

Hypalon 30 is made from a much lower molecular-weight polyethylene than Hypalon 20, and is also highly branched. The higher chlorine content (43%) gives a glass-transition temperature above ambient and produces hard glossy films with good oil and flame resistance. Its higher chlorine content also makes it more soluble in common solvents. It has the lowest solution viscosity of any commercial CSM and can therefore be used at high solids in solvent paints.

4.2. General-Purpose Grades

The five grades of Hypalon products based on HDPE at around 35% chlorine may be considered general-purpose elastomers. They are used in hose, tubing, electrical wiring, industrial rolls and belts, molded and sheet goods, as well as many other extruded applications. The linear structure provides good mechanical properties and processability. Heat and oil resistance is better than the branched types because of the absence of tertiary chlorine atoms and higher chlorine content in the amorphous region. They have good ozone, flame, abrasion resistance, and insulating properties, but their principal uses result from their excellent combination of heat and oil resistance with a balance of good mechanical and processing properties. Figure 3 shows the general position of these types in relation to other general-purpose elastomers (25). Hypalon 40 is a medium viscosity type and is the most versatile of the group. Hypalon 40S and Hypalon LD999 have lower viscosities than Hypalon 40 and are often used to customize compound viscosity to improve processability. Hypalon 4085 and Hypalon 610 are higher in molecular weight and are useful where higher uncured integrity, during processing, is needed, ie, pan-cured hose. They are made from very narrow MWD polyethylene which allows high extension with fillers and plasticizers to reduce costs while retaining good mechanical properties in the cured product.

4.3. High Chlorine Grades

Hypalon 48 is a high chlorine grade with a high glass-transition temperature, making it a more plastic material than the general-purpose grades. Oil resistance is equivalent to low grades of nitrile rubber, but heat resistance and low temperature flexibility, although better than nitrile, are poorer than other CSM types. It is made from HDPE, which imparts toughness making it useful in some uncured applications, but its most important uses

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are in automotive and air conditioning hose, where it has very low permeability to Freon fluorocarbons. Low solution viscosity also makes it useful in some coatings applications where its dry slick finish is advantageous, ie, auto door and window strip coatings.

4.4. Low Chlorine Grades

Hypalon 45 and 623 are used mostly in unsupported roofing membranes and pond liners. The low chlorine level along with special control of reaction conditions provide high levels of polymethylene blocks which produce high crystallinity to give high strength uncured compounds. They can be compounded with white or light-colored pigments and calendered into uncured sheet with sufficient strength to be applied as a sheet roofing or pond liner. Since it is uncured, the overlapped seams can be solvent welded or heat-sealed to give a continuous film. A small amount of divalent metal oxide added to the compound provides a slow ionic cure when the membrane is in place and exposed to moisture, adding to long-term strength. Hypalon 623 is a low viscosity variant designed for easier processing. The CAS Registry Number for Hypalon 623 [103170-38-3] indicates a 1-octene polymer with ethene, chlorosulfonated. The octane content of the base resins, however, is very low (0.5–1%) having a density of about 0.95 vs 0.92 for LLDPE. Both Hypalon 45 and 623 contain a chlorine content balanced to give excellent weatherability and low temperature flexibility. When properly compounded, they can be calendered into smooth sheets and rolled for easy application. Hypalon 45 roofs have been found to have good integrity after 20 years weather exposure. Their weather resistance in light pastel colors has made them especially useful in architectural roofing.

4.5. Acsium Grades

Alkyl CSM, ACSM, or Acsium polymers, based on linear low density polyethylene, represent a new class of CSM specifically designed for applications requiring excellent dynamic properties over a broad temperature range, ie, auto timing and accessory drive belts. Hypalon 40 or LD999 have adequate heat and oil resistance for these applications, but have neither low temperature flexibility nor dynamic property requirements. For CSM these properties are dependent almost entirely on chlorine content and state of cure. Introduction of pendent, short alkyl groups on the polymer backbone allows reductions of chlorine content without interference from crystallinity (25, 26). By adjusting reaction conditions for selective chlorine distribution and using LLDPE (0.92 density), as a source of pendent alkyl groups, it is possible to lower the chlorine content to about 26% without significant crystallinity. ACSIUM 6367 and ACSIUM 6983 are optimized by low chlorine content for low hysteresis and high resilience. The low T_g also gives good low temperature flexibility. The crystallinity of these polymers is very low ($\Delta H < 4$ J/g). ACSIUM 6932, at 30% Cl, has a sufficiently high chlorine content to give oil resistance equivalent to CR at the expense of slightly higher hysteresis. Acsium polymers can be compounded to give greatly improved low temperature fracture resistance, resilience, damping, and heat resistance over standard CSM grades. Whereas the PE base for Hypalon 623 contains <1% (usually <0.5%) octene comonomer, Acsium grades may contain comonomers other than octene, ie, hexene, butene, or combinations. Actual compositions are considered proprietary by Du Pont.

4.6. Hypalon CP Grades

These represent a family of polymers closely related to CSM in that addition of chlorine to precursors other than polyethylene add value as modifiers for adhesives, coatings, and inks because of increased solubility and compatibility.

4.6.1. Hypalon CP-700

In response to the need to reduce the amount of volatile organic solvents used in the application of many coatings and adhesives, Du Pont introduced a line of low molecular-weight chlorosulfonated polyethylene resins. Coded Hypalon CP-700, these resins maintain the same characteristics as the high molecular-weight Hypalon resins they are designed to replace (Hypalon 20 and 30), eg, flexibility, solvent, and chemical resistance and wet adhesion, but can be formulated into considerably higher solids formulations. This significantly reduces the amount of solvent required for their application. Since these are low molecular-weight materials ($M_w \sim 3000$), cure systems needed to be developed to assure that the resins would be able to perform equivalent to their higher molecular-weight predecessors. Several cure chemistries have been developed for Hypalon CP-700 resins including amino-alkoxy silanes, polyamine and polyepoxy, polyol and polyisocyanate, polyamine and polyisocyanate, and redox acrylics. The performance of the cured Hypalon CP-700 resins has been shown to equal or exceed that of similar coatings prepared with the high molecular-weight Hypalon resins alone.

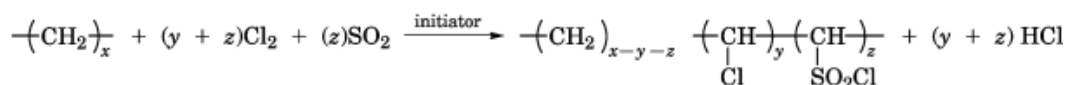
4.6.2. Hypalon CP 826

This is a chlorinated, maleic anhydride modified polypropylene having a chlorine content of about 25% and maleic anhydride content of about 0.8%, developed to promote adhesion of inks and coatings to polypropylene or blends containing polypropylene. It has a solution viscosity of 125mPa·s (= cP) at 20% solids in xylene and can be used in dilute solutions as a wash primer or a tie layer between materials that are difficult to adhere. CP 827 is a higher molecular-weight analogue with a solution viscosity of 280mPa·s (= cP) at 20% solids in 80/20 xylene/methyl isobutyl ketone.

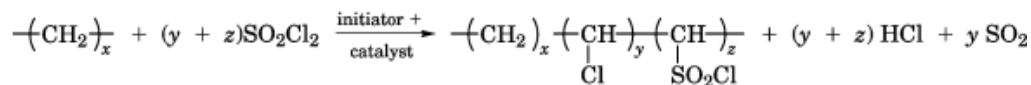
5. Manufacture

Unlike most elastomeric polymers, which are made by direct polymerization of monomers or comonomers, chlorosulfonated polyethylene, as the name implies, is made by chemical modification of a preformed thermoplastic polymer. The chlorination and chlorosulfonation reactions are usually carried out simultaneously but may be carried out in stages.

A simplified form of the reaction may be represented by



or



The initiator is usually an azo compound and the sulfonation catalyst is usually a tertiary amine, ie, pyridine. Sulfuryl chloride and chlorine may be used without the sulfonation catalyst to produce the same product. Values for x , y , and z are variables and help determine the various product grades.

A number of preparation schemes for CSM have been demonstrated on a laboratory or pilot-plant scale, including fluidized-bed (27), stirred dry powder chlorosulfonation (28), dispersions of fine powders in a non-aqueous medium (28), melt/extrusion (29), falling films or powders (30), and various solution processes both batch and continuous reaction (30–32). The only process of current commercial significance is a solution batch process operating at pressures of 1–350 kPa (0–50 psig). For this process, the solvent must dissolve both the

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polyethylene and the final product, be essentially inert toward chlorinating agents, have a boiling point such that very high pressures are not required to maintain single-phase reaction, and such that it can be removed below the decomposition temperature of the CSM. Many solvents have been used in laboratory studies, ie, chlorobenzene ((33, 34)), 1,1,2,2-tetrachloroethane, trichlorofluoromethane, and chloroform, but only carbon tetrachloride ((33–35)) or mixtures with other solvents (36) have been of significant commercial importance in batch units.

Carbon tetrachloride is toxic and an experimental carcinogen requiring stringent environmental control measures. It was placed on the Montreal Protocol list of potential ozone depleting agents in 1989, and its manufacture is scheduled to be completely phased out by the year 1996. It is likely to be replaced as a chlorosulfonation medium by chloroform, not currently considered an ozone depleting agent, or other nonozone-depleting agents which may also be nontoxic noncarcinogens.

The chlorosulfonation reaction is carried out with a mixture of sulfur dioxide and chlorine (37), sulfuryl chloride and chlorine (38), or sulfuryl chloride and a catalytic amount of an organic base (35, 37).

The commercial manufacture consists of charging polyethylene pellets into a glass-lined stirred reactor kettle fitted with an agitator and at least one condenser. Staged condensers are sometimes used for improved reaction temperature control. The reactor is then closed and pressurized to about 200 kPa (2 atm). Superheated (150°C) dry CCl_4 is added under pressure, with agitation, such that the polyethylene is dissolved at the end of solvent addition. For high density polyethylene, the dissolving temperature is at least 98°C. The chlorosulfonating agents and free-radical initiator, usually 2,2'-azobisisobutyronitrile, are fed continuously during reaction. The heat of reaction, about 54 J/g (13 cal/g), is removed by condensing solvent vapors and returning the cooled reflux to the reaction vessel. When sulfuryl chloride is the chlorosulfonating agent, the total heat balance is negative resulting in a decrease in temperature during the reaction cycle. The by-product HCl and SO_2 are vented through the condenser and neutralized or optionally mixed with make-up Cl_2 , equimolar to the SO_2 content, and passed through an activated carbon reactor to produce sulfuryl chloride for further use as a chlorosulfonating agent. Control of the reaction temperature is important in determining the polymer product chemical composition. Low reaction temperatures aid in increasing polymer S to Cl ratio. When the desired composition is reached as determined by ir analysis, the by-product HCl and SO_2 are removed by decreasing the reaction pressure to atmospheric or a slight vacuum. An epoxy resin stabilizer is then added to scavenge remaining amounts of HCl and to provide storage stability for the final product.

Solvent removal has been accomplished on a commercial scale by steam distillation (39), extraction/extrusion (40), or drum drying (41). The most common isolation procedure, drum drying, involves evaporation on steam heated double-drum surfaces at temperatures of 150–170°C. The counter-rotating drums are set to form a boiling pool of polymer solution above the drums. A thin film of polymer-rich solution is deposited on the drum surface and the remaining solvent is evaporated as the drum rotates through the bite. The dried film, containing <0.2% solvent is removed with a doctor blade to form a sheet that is gathered into a rope, conveyed, and cut into small pieces called chips. The chips are dusted with antimassing agent and packaged in reinforced and polyethylene-lined 25-kg paper bags. The packaged product is shipped by boxcar or trucks.

Process and environmental air is compressed and passed through activated beds to reduce air emission levels to <5 ppm. Process wastewater is air stripped to remove CCl_4 . The solvent containing air is also passed through the activated carbon beds. The total air flow through the beds averages about 3965 m^3/min (140,000 SCFM).

6. Economic Aspects

Production of chlorosulfonated polyethylene products on a worldwide basis is estimated to be approximately 50,000 t/yr. The Du Pont Co. is the primary manufacturer with one plant in the United States having a capacity of about 33,000 t and one plant in Northern Ireland with about 13,000 t capacity. The remaining world capacity

is provided by Toyo Soda Manufacturing Ltd. in Japan. The Du Pont Co. manufactures all CSM types under the trade names of Hypalon and Acsium Synthetic Rubber at each of its plant sites. Toyo Soda makes closely related products under the trade name CSM-CP, or Ts. Since the precursor material is primarily ethylene, materials costs are related to petroleum prices. Costs of environmental control procedures surrounding the use of carbon tetrachloride solvent have escalated extensively because it was placed on the Montreal Protocol of potential ozone depleting agents in 1989. Because carbon tetrachloride is to be completely phased out by the year 1996, significant investment in new equipment designed to handle replacement solvents is anticipated. General-purpose grades of CSM, ie, Hypalon 40, have a selling price of \$2.80–3.00/kg whereas special grades, ie, Acsium, sell for about \$7.70/kg. Average selling prices of all CSM grades is about \$3.50/kg.

7. Health and Safety Factors

Hypalon may contain small amounts of carbon tetrachloride residue and a much lesser amount of chloroform. These chemicals are toxic and carcinogenic with TWA exposure limits of 5 ppm. Both are regulated as air contaminants in the United States under the Occupational Safety and Health Act (OSHA) (42). When large quantities of raw polymer are stored or processed, it is advisable for protection of personnel to provide adequate ventilation to keep employee exposure below regulated levels. Significant amounts of sulfur dioxide and hydrogen chloride may also be evolved during mixing or processing.

Hypalon raw polymer compounds or cured product may be disposed of in an approved landfill. Incineration is not recommended because of the evolution of toxic gases. Additional information is available from Du Pont concerning these and other potential health hazards when handling Hypalon compounds, finished products, thermal decomposition products, or waste disposal (43).

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