POLYCHLOROPRENE

1. Introduction

Polychloroprene [9010-98-4] was discovered in 1930 at E. I. du pont de Nemours & Co. in Wilmington Delaware. The discovery grew out of a need to develop a synthetic substitute for natural rubber. DuPont first marketed this first commercially successful synthetic elastomer as DuPrene in 1933. In response to new technology development that significantly improved the product and manufacturing process, the name was changed to neoprene in 1936. The current commercially acceptable generic name for this class of chlorinated elastomers is CR or chloroprene rubber.

Since the time of its introduction to the marketplace, neoprene has been more than a simple replacement for natural rubber. Like natural rubber, neoprene is rubbery, resilient, of high tensile properties. However, neoprene has better heat stability, better resistance to varying environmental weathering conditions, superior flex life, excellent solvent and oil resistance and reasonable electrical properties when compared to natural rubber. This unique combination of properties poised neoprene for solving many of the potential problems besetting the automotive, construction, footwear, specialty apparel, transportation, and wire and cable industry. The good balance of properties has made the polymer useful in a large divergent list of applications including aircraft, appliance, automotive, bridge pad, chemical resistant clothing, home furnishings, machinery, mining and oil field belting, underground and undersea cables, recreation, and tires.

2. Polymerization

Chloroprene, 2-chloro-1,3-butadiene, [126-99-8] monomer undergoes dimerization and autopolymerization when stored at ordinary temperatures. These reactions occur simultaneously by different mechanisms. Free-radical processes normally initiate autopolymerizations. The dimerization reactions are thermally initiated.

2.1. Dimerization. The dimerization reactions follow second-order kinetics and involve $2+2$ and $4+2$ concerted and non-concerted cycloaddition reactions. Alternative mechanisms involving Cope rearrangements account for the formation of dichlorocyclooctadiene. The rate of dimer formation is affected both by temperature and monomer concentration. Due to the high (20.9–24 kcal/mole) activation energy, storage tank temperature is a powerful tool for controlling rates of dimerization (1,2). Free-radical inhibitors do not inhibit chloroprene and dichlorobutadiene dimerization (3–6). As dimerization is one of the major sources of exothermic heat of reaction, storage vessel temperature control is of primary concern in avoiding uncontrollable runaway reaction during commercial monomer synthesis and storage of chloroprene and dichlorobutadiene. Dilution of monomer with inert solvents aids the safe shipment of these reactive monomers.

2.2. Free Radical Polymerization. Autopolymerization of chloroprene monomer occurs readily under free-radical and photochemical conditions. The electron-rich and electronegative chlorine atom facilitates the high reactivity of this monomer. Over the temperature range 20–80 °C, the initiation depends on formation of di-radicals or added free radical that initiate polymerization. Polymerization proceeds at a rate that follows first-order kinetics with activation energy of 82 kJ/mol (19.6 kcal/mol) and heat of polymerization of 68–75 kJ/mol (16–18 kcal/mol) (1,3,7,8).

$$k(p) = 4.8 \times 10^{-8}\,\mathrm{s}^{-1}$$

Bulk Polymerization. The rate of bulk polymerization is strongly catalyzed by peroxides such as cumene hydroperoxide or chloroprene peroxides. Chloroprene peroxides are formed either by deliberate or adventitious exposure of monomer to oxygen (4,9). Maynard showed that less than 0.1% polymer was formed when specially purified chloroprene monomer was allowed to age in the dark at ambient temperatures for eight weeks. When chloroprene monomer was exposed to 0.1-mole % oxygen and aged in a similar manner, 19% polymer was formed in only three days. Thus oxygen absorption leading to peroxide formation is a major safety concern for large-scale manufacture and storage of chloroprene and dichlorobutadiene. Thiodiphenylamine (0.05%) mitigates the problem by reducing oxygen absorption rate at 25 °C by more than four-orders of magnitude.

Emulsion Polymerization. Commercial polymers are made by aqueous batch, semicontinuous (semibatch), or continuous free-radical emulsion polymerization. The emulsion system is composed of five components: monomer, surfactant, water, chain transfer agent, and initiator (2). Organic fatty acid salts, sulfonic acid salts or substituted diterpene salts (sodium abietate) derived from synthetic or natural (eg, pine trees) sources constitute the surfactants most commonly employed to stabilize the colloid for emulsion polymerization. Water forms the continuous phase that provides low emulsion viscosity, aids in heat transfer, and compartmentalizes polymerization to allow rapid formation of high molecular weight polymer where branching can be effectively controlled. Emulsion polymerizations are faster than bulk, solution or suspension and yield polymers having a much higher molecular weight (10). When used at 0.01–1.5 weight % concentrations, dodecylmercaptan, iodoform, or dialkyl xanthogen disulfides are efficient chain-transfer agents. The molecular weight of chloroprene sulfur copolymers is controlled by a different strategy. Copolymerization of chloroprene with 0.1–2% sulfur followed by cleavage and capping thionyl ends with a combination of 1.0–5.0% tetraethyl thiuram disulfide and 0.25–2.0% sodium dibutyl dithiocarbamate yields a polymer having number average molecular weight that range up to 500 M atomic mass units (11).

Polychloroprene emulsion polymerization follows Smith-Ewert kinetics developed initially for polystyrene (2). After mixing the monomer, water and surfactant by under high shear, the surfactant molecules will cluster into monomer-swollen micelles and monomer droplets. The micelles number 10^{17}–10^{18} micelles dm^{-3} having diameter ranging from 50 to 150 ^{0}A. The bulk of the monomer resides in the surfactant-stabilized monomer droplets that number 10^{9}–10^{11} dm^{-3} with particle diameter ranging from 1 to10 micrometers. The initiators are generally formed *in-situ* by redox reactions of oxidants such as alkali persulfates or peroxides and reducing agents such as alkali sulfites, reducing carbohydrates, or reducing acids. Upon addition of the initiator to the emulsion, free radicals are formed in the emulsion aqueous phase at a rate of $10^{16}-10^{18}$ radicals dm^{-3} s^{-1}.

Harkins's theory suggests that emulsion polymerization occurs in three intervals. During interval I, or the particle formation phase, the free radicals from initiators either react with monomer in the aqueous phase to propagate oligomeric chains (homogeneous nucleation), enter the micelles to initiate polymerization (micellular nucleation) or less frequently initate polymerization in the much larger and sparser monomer droplets (droplet nucleation). As polymerization continues all micelles continue to grow and are ultimately converted into polymer particles signaling start of Interval II. During interval II, the polymer particles continue to grow as more monomer diffuses from the droplets to the locus of polymerization. When all monomer has diffused from the droplets to the particles, the monomer droplets disappear signaling the beginning of interval III. During interval III, polymerization rates initially decrease as the concentration of the monomer has been reduced significantly. At the latter stages of interval III, polymerization rates increase again (Tromsdorff gel effect) due to decreased termination frequency of growing radicals resulting from high internal viscosity (12). At a desired conversion of the monomer, the polymerizations of mercaptan, iodoform, and xanthogen disulfide modified polymerizations or chloroprene/sulfur copolymerizations are quenched with the aid of hindered phenols, alkyl hydroxylamines, or thiodiphenylamine. Typically emulsion will contain 30–60% solids at the end of polymerization.

In addition to electrostatic colloid stabilization generated by anionic surfactants, liquid dispersions are also made from nonionic surfactants. Stabilization of the emulsion is achieved by electrosteric stabilization or by pure steric stabilization (2,13). Polyoxyethylene dodecyl ethers, polyoxyethylene nonyl phenyl ethers, and polyoxyethylene nonyl phenol ethers are a few surfactants typically used in emulsion polymerization with nonionic surfactants (14–16). Nonionic emulsion polymerizations are characterized by lower critical micelle concentration than the ionic counterparts. Thus the emulsion particle sizes are generally much larger in the ionic polymerizations. The mechanism of radical entry and exit is polymeric surfactant stabilizer systems are different than in anionic systems. With water-soluble initiators, the kinetics depend on initiator concentration.

Chain Transfer. In emulsion polymerization, polymer chains grow rapidly to very high molecular weight. The ultimate polymer molecular weight can, however, be conveniently controlled by chain-transfer agents (AX). A chain-transfer agent, AX intercepts a growing polymer radical.

$$\mathrm{Rn}\bullet + \mathrm{AX} \xrightarrow{k_{tr,AX}} \mathrm{RnX} + \mathrm{A}\bullet$$

$$\mathrm{A}\bullet + \mathrm{M} \xrightarrow[\text{fast}]{k_{p,A}} \mathrm{R}_1\bullet$$

The active center of the chain transfer agent reacts with the growing chain to stop further chain propagation. A new free radical, A, is formed from the chain-transfer agent. The new free radical initiates a second polymer chain by reacting with more monomer, M. Thus the ultimate polymer molecular weight depends on the concentration of chain transfer agent (17).

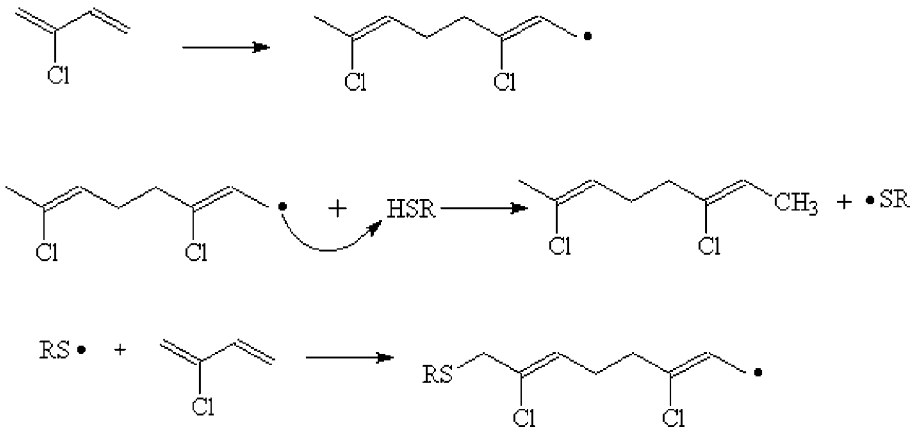
There are at least two conditions that define a chain-transfer agent. A compound becomes a chain-transfer agent if the rate of polymer chain propagation exceeds the rate of chain transfer.

$$k_p[M] >> k_{\mathrm{tr,AX}}[AX]$$

This condition allows the polymer chain to propagate to high molecular weight. Secondly, the rate constant for polymer chain propagation, k_p, must be of similar magnitude to the rate constant for re-initiation of the polymer chains by the chain-transfer agent (17). In instances where one or the other condition is not satisfied, the agent could be considered an inhibitor.

$$k_p \geq k_A$$

Thios (eg, dodecyl mercaptan), halogenated compounds (eg, CBr_4, CCl_4) and activated disulfides such as xanthogen disulfides are normally employed in commercial polychloroprene polymerization.



The mechanism of this series of reactions involving dodecyl mercaptan chain transfer during a high pH polymerization was elucidated using radio-sulfur tagged dodecylmercaptan (18). The use of multiple chain-transfer agents of different reactivities yielded polymer of more uniform structures (19).

The chain-transfer rate constants, k_{tr}, are determined from average molecular weight in a polymerizing system. The intercept of a Mayo plot of number-average-molecular weight against $[I]/R_p$ where $[I]$ is the initiator concentration and R_p is the polymerization rate (20). Extensive compilations of k_{tr} values are found in the open literature (27). Dodecyl mercaptan is used in the manufacture of commercial Neoprene W. The chain-transfer rate constant for dodecyl mercaptan with chloroprene was determined using the Mayo plot technique (22) as follows:

$$k_{\mathrm{tr,DDM}} = 368\,\mathrm{dm^3 mol^{-1}\,s^{-1}} \quad \text{at} \quad 40^{\circ}\mathrm{C}$$

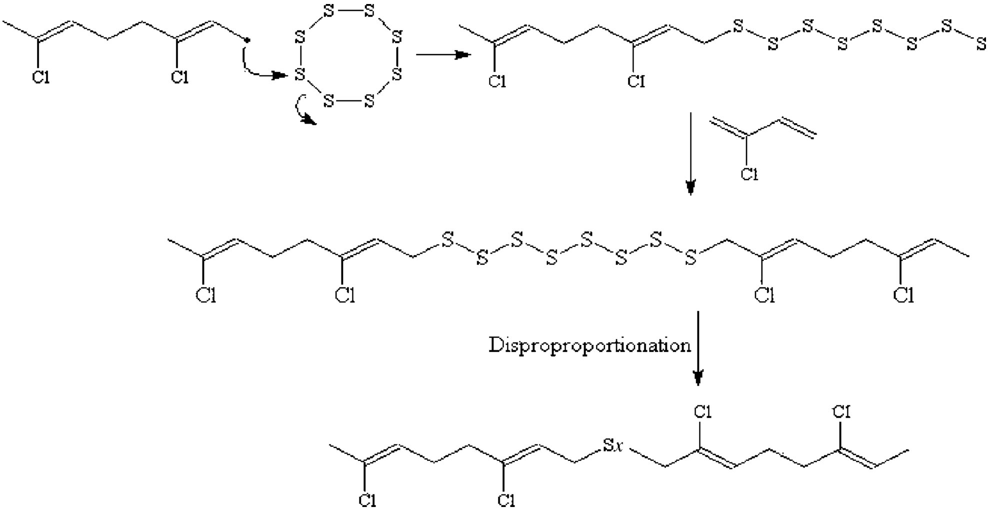
The choice of chain-transfer agents can have an impact on vulcanizate properties. Mercaptan chain transfer agents yield polymer having nonreactive and dangling end groups. Xanthogen disulfide chain transfer agents produce polymers having reactive end groups that participate in the vulcanization reaction, contribute to the network structure and thereby contribute to high modulus of the polymer.

2.3. Copolymerization. In free-radical copolymerizations, the composition of the copolymer is controlled by the comonomer reactivity ratios (23). The monomer reactivity ratio is defined as the quotient of the rate constants for chain homo-propagation to the rate constant for chain cross-propagation.

$$r_{\mathrm{A}} = k_{\mathrm{AA}}/k_{\mathrm{AB}} \quad r_{\mathrm{B}} = k_{\mathrm{BB}}/k_{\mathrm{BA}}$$

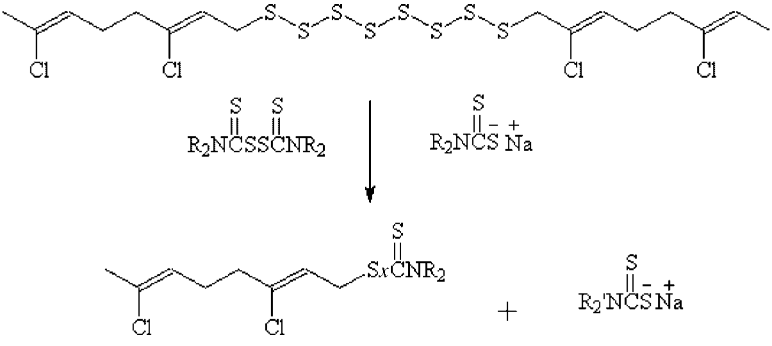
The expressions are an outcome of the “terminal model” theory with several steady-state assumptions related to free-radical flux (14,23). Based on copolymerization studies and reactivity ratios, chloroprene monomer is much more reactive than most vinyl and diene monomers (Table 1). 2,3-Dichloro-1,3-butadiene is the only commercially important monomer that is competitive with chloroprene in free radical copolymerization rate. 2,3-Dichlorobutadiene or ACR is used commercially to give crystallization resistance to the finished raw polymer or polymer vulcanizates. α-Cyanoprene (1-cyano-1,3-butadiene) and β-cyanoprene (2-cyano-1,3-butadiene) are also effective in copolymerization with chloroprene but are difficult to manage safely on a commercial scale. Acrylonitrile and methacrylic acid comonomers have been used in limited commercial quantities. Chloroprene–isoprene and chloroprene–styrene copolymers were marketed in low volumes during the 1950s and 1960s. Methyl methacrylate has been utilized in graft polymerization particularly for vinyl adhesive applications. A myriad of other comonomers have been studied in chloroprene copolymerizations but those copolymers have not been used with much commercial success.

Chloroprene-Sulfur Copolymerization. The high reactivities of chloroprene and dichlorobutadiene permit copolymerization with sulfur to yield toluene-insoluble and partially gelled copolymers of high molecular weight. Gelled polymers are highly crosslinked polymers that are insoluble in toluene. In solution or aqueous emulsion polymerization, a growing polychloroprene radical reacts with rhombic (nonpolymeric) sulfur (24) or suitable sulfur donors such as 1,2,3,4-tetrasulfocyclohexane (25) or polysulfides (26) to yield a copolymer. Reaction with elemental sulfur involves cleavage of the eight-membered sulfur in a ring opening reaction to yield a thionyl-terminated radical.



The radical will initiate another homopolymer chain by reaction with more monomer. Finally disproportionation occurs and the sulfur rank is reduced to 3–6 sulfur atoms per block unit. The average number of sulfur atoms between polychloroprene chains or sulfur rank has been explore by 1H nmr. The chemical shift of the methylene hydrogen atoms adjacent to the polythionyl linkages vary from 3.45 to 3.9 ppm (27). It is believed that the sulfur rank for a typical chloroprene–sulfur copolymer contains a predominance of S_3 to S_6 units. The assignment is consistent with ease of reaction of dialkyl polysulfides ($\mathrm{S}x > 2$) with the chemicals normally used the peptization reactions that follow.

In order for the chloroprene–sulfur copolymer to be useful for rubber processing and curing, the molecular weight or Mooney viscosity must be reduced to approximately 500,000 a.m.u. This molecular weight corresponds to approximately 45 Mooney viscosity where Mooney viscosity was determined according to ASTM D-1646-96A with a large rotor at 100 °C test temperature for five minutes total test time. Molecular weight reduction is achieved by cleaving the sulfur-sulfur bonds of the copolymer through a process termed peptization.



In solution or at the end of emulsion polymerization, tetraalkyl thiuram disulfides are added to the emulsion. Very little reaction occurs at this point. Alkali metal salts of dithiocarbamates, secondary amines or alkali salts of mercaptobenzothiazole (28) are added to initiate the peptization reaction through sulfur–sulfur bond cleavage. The polychloroprene sulfide ion reacts with the tetraalkyl thiuram disulfide to cap the end of the polymer and generate a second dithiocarbamate salt. The second dithiocarbamate salt propagates the peptization reaction. Thus the final polymer molecular weight and bulk Mooney viscosity will depend on initial sulfur concentration in the copolymerization and the concentration of tetraalkyl thiuram disulfide and dithiocarbamate salt added during the peptization step.

Interpenetrating Polymer Networks (IPN). Polymerization of vinyl and diene monomers over an already formed molecule held in a polymer particle represents a special case of copolymerization. The interpenetrating polymer networks thus formed overcome many of the miscibility and other problems associated with physical blends of individual copolymers and leads to new compositions that are useful for coatings, adhesives, and caulks (14). Polychloroprene IPNs have been made by co-curing copolymers of 1-chloro-1,3-butadiene [627-22-5]. The 1-chloro-1,3-butadiene comonomer polymerizes in a fashion to increase the allylic chloride concentration in the copolymer backbone. The butadiene copolymer with 1-chloro-1,3-butadiene (29) and octyl acrylate copolymer (30) improved the low temperature brittleness, oil resistance, and heat resistance of polychloroprene.

Block Copolymers. Block copolymers have been made in two-step processes. First a mixture of chloroprene and *p*-xylene-bis-*N*,*N*′-diethyl dithiocarbamate was photopolymerized to form a dithiocarbamate terminated polymer which was then photo-polymerized with styrene to give the block copolymer. The block copolymer had the expected morphology of spherical polystyrene domains within the polychloroprene matrix (31). Other routes to block copolymers involved hydrolysis of xanthate or thiocarbamyl end capped polymers followed by oxidative coupling of the two different homopolymers. Core-shell technology is another potential route to block copolymers.

Graft Polymerization. Graft polymerization is related to block copolymerization. A block copolymer contains long sequences of two monomers (ie, AAA monomer blocks followed by BBB monomer blocks) along the copolymer chain. Graft copolymers consist of long chains of one monomer with occasional branches consisting of long chains of a second (grafted) comonomer. The branched points are normally formed by allylic atom (typically hydrogen) abstraction by free-radical initiators (eg, peroxides) to yield a resonance-stabilized free radical. The free radical initiates the addition polymerization of a second monomer beginning at the locus of the free radical. Generally grafting is performed to significantly modify polymer properties. In the production of emulsion-polymerized acrylonitrile–butadiene–styrene tripolymer, styrene and acrylonitrile are grafted onto rubbery polybutadiene to improve compatibility between the thermoplastic and rubber matrix used in impact modification (12). Methyl acrylate, acrylonitrile, alkyl methacrylates (eg, methyl, octyl, lauryl), fumaronitrile, methacrylic acid, and dichlorobutadiene have been employed in solution and emulsion graft polymerization with polychloroprene. Generally, solvent resistance, heat resistance, and hydrolytic resistance were improved. Solution graft polymerization of methyl methacrylate to polychloroprene is a commercially important process for making adhesives finding utility for bonding to vinyl containing plasticizers that migrate to the surface of the substrate with time.

2.4. Other Modes of Polymerizations. *Popcorn Polymerization.* ω-Polymerization frequently referred to as popcorn polymerization due to the physical appearance of the polymer, can be a dangerous side reaction for monomer storage vessels. The polymerization appears to proceed without external initiation (32–34), and is catalyzed by the tightly gelled polymer seeds that are a product of the polymerization. Once seeds are present and immersed either in the liquid or vapor phase of monomer, their weight increases exponentially with time.

Fresh radicals are formed continuously by mechanical rupture of the polymer chains that are swollen by dissolved monomer (32,35). Termination of polymer radicals, in turn, is inhibited by the rigidity of the polymer network. The reaction is temperature sensitive, and can be minimized with adequate cooling (32). On the other hand, heat transfer may be impaired as the mass of material grows. Polymerization continues until the available monomer is consumed or gross amounts of inhibitor are added to the system.

A number of inhibitors such as organic nitrites, nitroso compounds (32) oxides of nitrogen (36), alkali metal mercaptides (37), or nitrogen tetroxide adducts with unsaturates (38,39) have been recommended. The best control, however, is routine inspection and clean out of equipment to eliminate seeds.

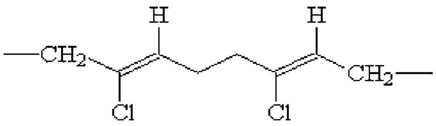
Nonfree-Radical Polymerization. Nonradical polymerizations have not produced commercially useful products, although a large variety of polymerization systems have been studied. The structural factors that activate chloroprene toward radical polymerization often retard polymerization by other mechanisms.

Cationic polymerization with Lewis acids yields resinous homopolymers containing cyclic structures and reduced unsaturation (40–42). Polymerization with triethylaluminum and titanium tetrachloride gave a product thought to have a cyclic ladder structure (43). Anionic polymerization with lithium metal initiators gave a low yield of a rubber product. The material had good freeze resistance compared with conventional polychloroprene (44). Alternating copolymers of chloroprene have been prepared from a number of donor acceptors complexes in the presence of metal halides. Frequently this enables preparation of copolymers from monomers having unfavorable reactivity ratios in radical polymerization. Triethylaluminum sesquichloride with a vanadium oxychloride cocatalyst yielded alternating copolymers of chloroprene with acrylonitrile, methyl acrylate, and methyl methacrylate when equimolar amounts of the two monomers were used (45). Polymer composition tended to follow the composition of the monomer mixture (46). The chloroprene units were shown to be in the trans-1,4-configuration (46) on the basis of infrared spectra. Variables affecting the acrylonitrile copolymerization were studied in detail (47) by infrared spectra. The alternating copolymer of acrylonitrile and chloroprene is resinous. A copolymer containing 35-mole % acrylonitrile was a soft, oil resistant elastomer (47): Stability constants have been determined for complexes of acrylic monomers with ethylaluminum sesquichloride, and related to the kinetics of copolymerization with chloroprene (48). Kinetic data have been determined for polymerization in the presence of a manganese cocatalyst (49).

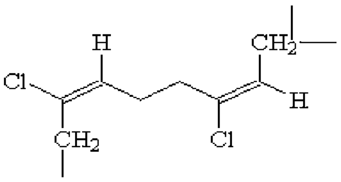
A series of graft polymers on polychloroprene were made with isobutylene, isobutyl vinyl ether, and α-methylstyrene by cationic polymerization in solution. The efficiency of the grafting reaction was improved by use of a proton trap, 2,6-di-*tert*-butyl pyridine (50).

3. Polymer Structure

3.1. Polymer Microstructure. Unsymmetrical diene monomers such as chloroprene polymerize by four reaction pathways: 1,4 head-to-head, 1,4-head-to-tail, 1,2 and 3,4 polymerization. The concentrations of microstructure vary with polymerization temperature (51). The *Z*-or trans-configuration predominates at conventional polymerizations carried out in the range of 10 to 45 °C.



zusammen, *Z*



entgegan, *E*

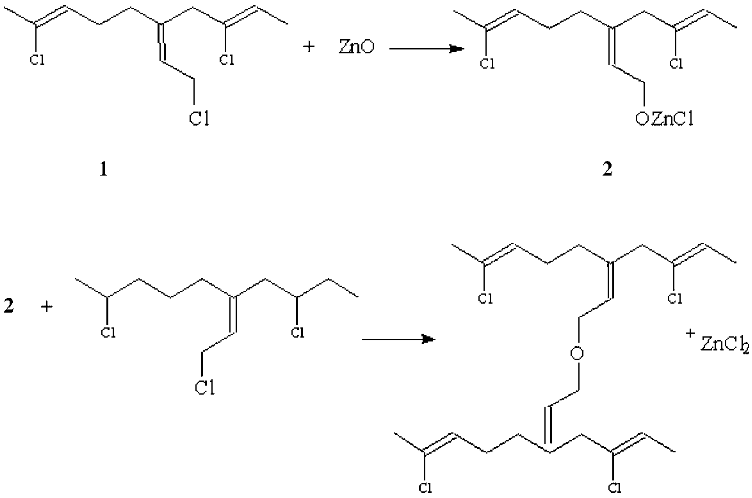
The concentration of *Z*-configuration varies indirectly proportional with the polymerization temperature whereas the other three configurations vary directly proportional with the polymerization temperature. The total amount of *E*, 1,2, and 3,4 configurations vary from 5% at −40 °C to 30% of the total polymer backbone at 100 °C polymerization temperatures. Other structural studies have involved 2,3-dichloro- butadiene homopolymer (52), the free-radical random copolymer with methyl methacrylate (53) with chloroprene and the alternating copolymer of sulfur dioxide with chloroprene (54).

Petiaud and Pham studied the thermodynamics of the various modes of unit addition (56).

The studies included: 1,4 Head-to-head polymerization leading to *Z* and *E* vinyl chlorides along the main chain; 1,4-Head-to-tail polymerization leading to *Z* and *E* vinyl chloride along the main chain; 1,2 polymerization leading to allylic chloride cure site; and 3,4 polymerization leading to vinyl chloride group.

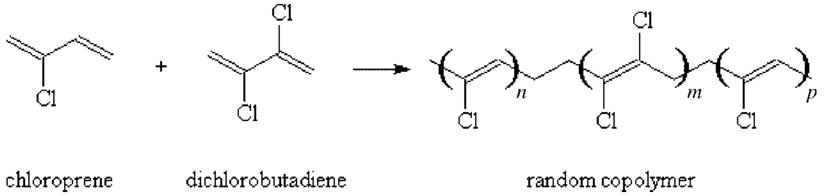
The four modes of polymerization result in microstructures that have profound effects on polymer properties and processability. The increased proportion of *Z*-configuration at low temperature leads to more stereoregular polymer chains that crystallize rapidly. This rapid crystallization rate results in a polymer of almost thermoplastic behavior. The polymer hardens rapidly at 25 °C and has utility for fast bond-developing adhesive applications. At intermediate and high polymerization temperatures, the higher concentrations of the allylic chloride, pendant vinyl chloride, and head-to-head and head-to-tail moieties provide a degree of crystallization resistance. As the Z-configuration is always in high concentration, polychloroprene polymers will crystallize under stress (eg, stretching) and providing increased strength to vulcanizates used as mechanical goods.

The allylic chloride moiety is the cure site for polychloroprene polymers. The reaction of the labile allylic chlorides with bifunctional nucleophiles, metal oxides, or thio ureas covalently join interpolymer chains into a polymer network. The polymer crosslink density is proportional to the concentration of allylic chlorides on the polymer backbone. Thus mechanical goods with high modulus are made from polymers of high allylic chloride concentration. On the other hand, high levels of allylic chlorides decrease the thermal stability of polychloroprene polymers per mechanism described for thermal degradation of unsaturated diene polymer (52,58)

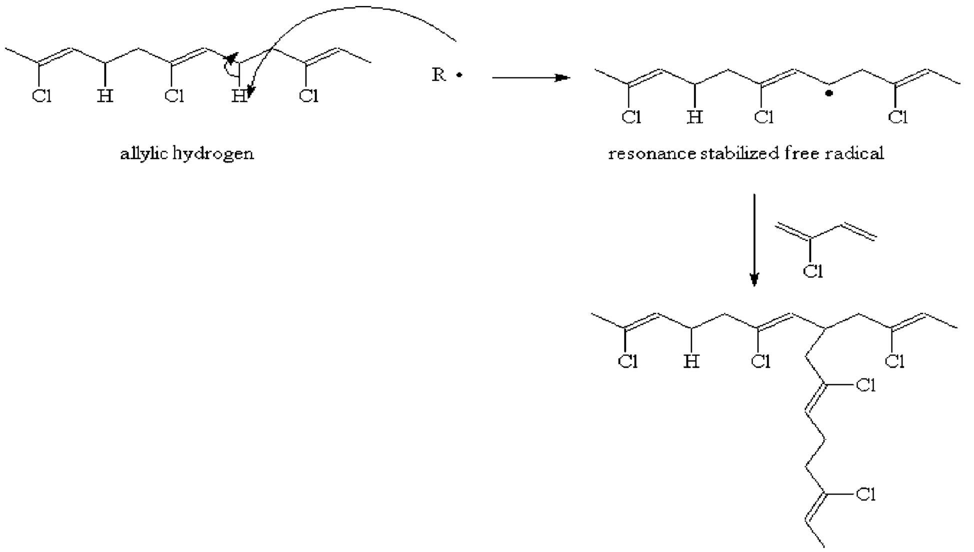


In 1964, Ferguson and co-workers conducted one of the first studies of microstructure by 1H nmr (15). They determined the relative proportion of head-to-head vs head-to-tail structures. The use of 350 MHz 1H nmr in $CDCl_3$ and C_6D_6 enabled quantitative analysis of head-to-head configurations along with the *E*-configuration (59). With the advent of ^{13}C nmr, a number of additional microstructures were observed. There was good agreement between earlier 1H nmr and ^{13}C nmr techniques (51,56,60–62). Other studies of microstructure have been conducted with the aid of infrared and Raman spectroscopy (63,64).

3.2. Copolymerization Microstructure. Dichlorobutadiene is the effective comonomer for polychloroprene copolymerization. The comonomer polymerizes in a 1,4 fashion leading to disruption of the *trans*-chloroprene segments in the polymer chain. Crystallization becomes difficult as polymer chains find it difficult to fit into crystalline lattices. Thus polymers containing dichlorobutadiene are very slow crystallizing. In fact, dichlorobutadiene is frequently referred to as ACR meaning Additive for Crystallization Resistance.



3.3. Branching. Branching is a special case of chain transfer. Instead of free-radical atom extraction from agents such as dodecyl mercaptan (DDM) or xanthogen disulfides, the extraction is from a preformed polymer chain. For polychloroprene, the chain transfer is to the allylic hydrogen atoms near the double bond. Upon free-radical extraction of the allylic hydrogen a new resonance stabilized free-radical is formed. This new free-radical initiates the growth of a new polymer chain that originates at the locus of the free-radical formation.



The formation of branched polymer originating at a resonance-stabilized free radical has precedence in the well-understood branching mechanism for vinyl acetate polymerization (65–67). Reaction of polymerizing chloroprene and vinyl acetate with ^{14}C-labeled model compounds was used to determine the relative kinetics of chain-transfer and double bond addition reactions with polymer. Chain transfer to allylic hydrogens or chlorine atoms on the polymer chain leads to long chain branching. Addition of the growing chain across a polymer double bond can lead directly to gel formation. Either reaction affects polymer rheology and processability. Vinyl acetate radicals, as a model for initiator fragments, were found to be 570 to 2,427 times faster in chain transfer reactions than chloroprene radicals. In all cases studied, the rate of double bond addition reactions were significantly faster than transfer reactions. Alternatively, rate of chain transfer can be determined by the method of Mayo (68).

The rates of chain-transfer to polymer and radical addition to double bonds of pre-formed polymers increase as a function of three variables: (*1*) temperature, (*2*) absence of chain transfer agent, and (*3*) with monomer conversion. Mochel (69) showed that that in the absence of a chain-transfer agent, up to 90% of the polymer formed at 30% monomer conversion was gelled.

There are several procedures for determining the extent of long-chain branching. Long-chain branching is accompanied by increased weight average molecular weight (Mw) as determined by gel-permeation chromatography (gpc)/ size exclusion chromatography (sec) or ultracentrifugation (70,71). The polydispersity (Mw/Mn) increases as branching increases. Branching has been quantitatively determined using 1H nmr (16,72).

The effect of branching on the zero-shear-rate intrinsic viscosity is often expressed in terms of branching index, g', defined as the ratio of the zero-shear-rate intrinsic viscosities of a branched to a linear polymer of the same composition and molecular weight.

$$g' = [\eta_0^{\mathrm{br}}/\eta_0^{\mathrm{linear}}]_M \leq 1$$

The zero-shear viscosity of a linear polymer is determined from the Mark-Houwick equation (73).

$$IV = KM^{\alpha}$$

where IV is the intrinsic viscosity, K is the Mark-Houwick coefficient, α is the Mark Houwick parameter.

The equation with pertinent constants for polychloroprene is used in determining the extent of branching. Thus, several linear polymers were made under extreme control conditions. The molecular weight distribution and intrinsic viscosities were determined for each polymer. A plot of ln(IV) vs molecular weight yielded α and K values:

$$IV = 1.95 \times 10^{-3} \times M^{0.542}$$

The universal calibration method was then used with gpc/IV method that involves dual detector measurement of both polymer concentrations by refractive index and solution intrinsic viscosity by capillary viscometry. The measurements provided full molecular weight distribution and branching distribution of the polymer. Polychloroprene polymers showed branching indices varying from 0.5 to near unity. Polymers designed for different end-use applications had different branching parameters that have been useful in predicting processability (74–76).

Chain-transfer agents such as dodecyl mercaptan or ethyl xanthogen disulfide inhibit long-chain branching and prevent any gel formation up to 60−70% monomer conversion (76). A bis-nonconjugated olefin such as ethylene glycol dimethacrylate is capable of network formation (insoluble gel) during free radical polymerization with chloroprene monomer (77). The branching index of such a copolymer would be near zero.

The extent of long-chain branching of a series of ethyl xanthogen disulfide modified polymers made at 40 °C and varying monomer conversion at showed that long-chain branching started near 56% conversion (76). As monomer conversion increased, branching and polydispersity increased. Finally near 82% conversion, the polymer gelled.

4. Polymer Manufacture

4.1. General Overview. Commercial polychloroprene rubber is manufactured by aqueous free-radical emulsion polymerization followed by isolation of the solid polymer by one of several processes: freeze roll isolation, drum drying (78), extruder isolation (79), precipitation and drying or spray drying (80,81). Isolation of powdered polychloroprene has been review (82). Of the methods cited, freeze roll and drum dry isolation are commercially important. The large-scale commercial manufacture of polychloroprene consists of eight or nine unit operations: (*1*) Monomer solution make-up, Water solution make-up; (*2*) emulsification; (*3*) polymerization; (*4*) stripping of residual monomer; (*5*) peptization for chloroprene–sulfur copolymers; (*6*) freeze roll isolation, drum drying; (*7*) drying of freeze-rolled film; (*8*) roping; and (*9*) cutting and packaging (25 kg)

A commercial manufacturing flowsheet is shown in Fig. 1.

4.2. Manufacture of Chloroprene–Sulfur Copolymer. The process for manufacture of a chloroprene-sulfur copolymer taken from the patent literature illustrates the batch process (84,85).

The monomer solution make-up involves addition and solubilization of elemental sulfur and rosin (substituted diterpenes) in the chloroprene monomer. The water solution is made in a second vessel. De-ionized water, sodium hydroxide and a dispersant, are mixed to form the water solution. The dispersant is a condensation product of naphthalene–sulfonic acid, and formaldehyde. The monomer and water solutions are mixed with centrifugal pumps to form an oil-in-water emulsion. The emulsion formed by virtue of formation of the sodium salt of rosin and resin components (abietic and dehydroabietic acids) having hydrophobic and hydrophilic ends. The large carbon-bearing portion of sodium abietate is hydrophobic and thereby solubilizes the monomer. The sodium carboxylate portion of sodium abietate is the hydrophilic end that extends into the aqueous phase and forms the electronic double layer that is critical to emulsion stability (80). In the patent example, the emulsion is added to the reactor and the temperature is increased to 40 °C polymerization temperature.

The reactors in modern commercial processes are brine jacketed, glass-lined, and fitted with a glass-lined agitator. Glass-line construction is important to prevent multivalent cations from contaminating the system, and precipitating polymer as coagulum.

Polymerization is initiated by addition of an aqueous potassium persulfate solution to the reactor. The emulsion temperature is maintained near 40 °C by control of a combination of three variables: (*1*) reactor jacket temperature, (*2*) agitator speed, and (*3*) catalyst addition rate. The progress of polymerization (87) was measured by specific gravity, which is continually monitored by computer in modern commercial processes. In the patent example, the initial monomer emulsion had 0.95 specific gravity. During polymerization, the specific gravity increased to a goal value due to continue formation of polymer having nominal

1.23 specific gravity. The free-radical polymerization was quenched at 91% monomer conversion (1.069 specific gravity) by the addition of a xylene solution of tetraethyl thiuram disulfide.

The emulsion is cooled to 20 °C. A dithiocarbamate salt or secondary amine is added and the emulsion aged for eight hours to peptize the polymer. The bulk Mooney viscosity of the polymer is thus reduced to levels suitable for rubber processing.

The emulsion or polymer dispersion containing flammable and toxic chloroprene monomer is next steam stripped with the aid of a turbannular stripper (88). The stripped emulsion contained less than 0.1% residual chloroprene monomer. At this point in the process, the emulsion can be further processed into a dry polymer or sold as a liquid dispersion.

Conversion to the dry polymer involves destabilization of the active surfactant, freeze coagulation, and drying. Thus, the stripped emulsion is acidified to pH 5.5–5.8 with 10% acetic acid solution. The surface-active behavior of the sodium rosinate surfactant is thereby effectively destroyed. The marginal colloidal stability of the emulsion is controlled exclusively by the naphthalene sulfonic acid condensate. Since the sulfonate is a salt of a strong acid it cannot be acidified by acetic acid. Acidified emulsion is contacted with the surface of a rotating chilled (−15 °C) stainless steel drum (ie, the freeze roll) thereby causing the polymer to plate or freeze out onto the drum. The coagulated film is skived from the roll by a stationary knife and conveyed to a woven stainless steel belt where it is thoroughly washed with water sprays to remove electrolytes and other impurities added or formed during polymerization. After washing, approximately 25% of the excess water and serum is squeezed from the film with the use of a squeeze roll. The film is then conveyed onto cloth covered aluminum girts where it is carried through an air circulating serpentine dryer having heating compartments with temperatures that range from 120 °C. The final dryer compartment operates near 50 °C to cool the dried film. The film is cooled further at the exit of the dryer by contacting a rotating cooling roll. In a modern commercial process, the film is gathered into a rope, conveyed to cutters where it is cut into small chips. The product is then packaged into bags weighing 25 kg polymer per bag.

In the patent examples, there are five key features that permitted freeze-roll isolation. The emulsion is of sufficient colloidal stability to prevent spontaneous coagulation before contacting the rotating freeze roll. The sulfonic acid salt is critical in that connection. The polymer has sufficiently low glass-transition temperature to prevent cracking from the freeze roll at typical (−15 °C) freeze roll operating conditions. The film maintains sufficient strength to be conveyed along the wash belt and through the dryer. In that connection, freeze roll isolation of very low Mooney viscosity polymers or fluid polymers is difficult or virtually impossible. The dryer cooling temperature and cooling roll temperature are controlled to prevent polymer cold flow leading to massing after the polymer has been packaged.

Continuous polymerization is a second process practiced on a large commercial scale (89). An illustrative example taken from the patent literature illustrates the continuous polymerization process. Thus a mixture of chloroprene, 2,3-dichloro-1,3-butadiene, dodecyl mercaptan, and phenothiazine (15 ppm) is fed to the first of a cascade of seven reactors. Water solution containing disproportionated potassium abietate, potassium hydroxide, and formamidine sulfonic acid catalyst are fed with the monomer solution to the first reactor. Polymerization initiates immediately. The emulsion is then cascaded to the second reactor and the process continues. The residence time in each reactor is 25 min at 45 °C. The emulsion exits the reaction train at 66% monomer conversion. In a second similar process, the catalyst is fed to each reactor along the reaction train.

The descriptions presented above are intended as an overview of polychloroprene technology as practiced over the commercial life of polychloroprene. Product and processes have changed since 1930 to meet changing consumer needs, to upgrade product quality, to improve the quality of the workplace and environment, to improve efficiency of operation, and to meet the demands of a changing global economy. The commercial chloroprene–sulfur copolymers were commercialized in 1937 (90). Low temperature polymerizations for adhesive applications were discovered in the late 40s. The mercaptan modified chloroprene homopolymers were commercialized in 1950. The crystallization resistant chloroprene–dichlorobutadiene copolymers were introduced in 1951. The fluid polychloroprene polymers were commercialized in the late 1950s. The sol/gel blends or "pre-crosslinked" grades were introduced in the 1960s for improved processability. Modifications to these basic types have continued into the 21^{st} century.

5. Properties of Polychloroprene Polymers

5.1. Crystallization. Some elastomers crystallize at temperatures that can significantly impact processing and vulcanizate behavior. Thus it is necessary to account for these behaviors when developing rubber compound formulations and processes. Crystallization is manifested by stiffening and hardening of the raw polymer, uncured compounded polymer, and the vulcanized polymer. Elastomers that crystallize will do so on stretching and thereby exhibit increased tensile strength. Those elastomers (eg, polychloroprene and natural rubber) will require less reinforcing fillers to develop strength than types that do not stress-crystallize (91). Crystallization is also enhanced by compression (Fig. 2). Frequently the profile describing the low temperature compression set as a function of time is S shaped indicating an initial period of nucleation followed by stress-induced rapid crystallization. The rates of crystallization of some polychloroprene commercial types follow a general trend: homopolymer > chloroprene–sulfur copolymer > chloroprene–sulfur–dichlorobutadiene tripolymer > chloroprene–dichlorobutadiene copolymer having higher levels of dichlorobutadiene (92). Finally, in addition to promoting stress-induced crystallization, polyester plasticizers will also increase crystallization rates. Presumably the ester plasticizers provide a medium for increased chain mobility that permits polymer chains to migrate to the preferred crystalline cells. Hydrocarbon oil plasticizers and co-blends with hydrocarbon rubbers will retard crystallization rates but may improve low temperature brittleness resistance.

Crystallization is important for some hose manufacturing applications as it imparts some stiffness for braiding. The rapid crystallization of some polychloroprene polymer is fully exploited in adhesive manufacture and use (55).

Crystallization of amorphous polymers is a time-dependent phenomenon. Polychloroprene crystallizes fastest at −12 °C (92,93). Below this temperature, thermal stiffening commences and restrains molecular motion and alignment. Crystallization rates and degree of crystallization are heavily impacted by several phenomenon of which polymer polymerization temperature and thermal history of the polymer sample before measurements are most important (Fig. 3).

Hardness increase, differential scanning calorimetry (dsc), differential thermal analysis (94–96), low temperature compression set, and Gehman torsional stiffness, are tests normally employed to measure crystallization properties. The heat of fusion of crystalline phase of polychloroprene homopolymer is approximately 96 kJ/kg (23 kcal/mole) and the activation energy for crystallization is 104 kJ/mole (25 kcal/mole). The extent of crystallization can be calculated from the density of amorphous polymer ($\rho = 1.23$), and the crystalline density ($\rho = 1.35$). Thus a polymer that is polymerized at −40 °C melts at 73 °C and is 38% crystalline. A polymer polymerized at +40 °C melts at 45 °C and is approximately 12% crystalline.

X-ray diffraction has also been used to measure crystallinity. X-rays diffraction analysis showed that the polychloroprene unit cell is orthorhombic, $a = 0.88$ nm, $b = 1.02$ nm, and $c = 0.48$ nm (97).

5.2. Heat Aging and Degradation. The weather and ozone resistance of polychloroprene vulcanizates are enhanced by the presence of chlorine atoms in the molecule. Thus polychloroprene is more resistant to environmental elements than natural rubber. In comparison to saturated elastomers, polychloroprene is less heat and oxidation resistant. H. C. Bailey studied the degradation of a mercaptan modified polychloroprene homopolymer and model compound (chlorooctene) under controlled temperature (90–120 °C), environmental chamber gas composition, and gas flow rates (58,93,98). Bailey concluded that as the polymer was oxidized hydrogen chloride was evolved at a rate that closely matched oxidation or oxygen uptake. Oxidation brought about both scission and crosslinking of the polymer and decreased the proportion of the polymer that was capable of crystallizing. In the early stages of oxidation, crosslinking occurred mainly through the formation of intermolecular peroxides. The activation energies for oxidation and accompanying dehydrochlorination were found to be 17.6 and 25.8 kcal/mole respectively for polychloroprene. Molecular weight determination showed that at low degree of oxidation, scission of polymer molecules predominated over crosslinking. Chain scission resulted from the decomposition of intramolecular peroxides and hydroperoxides with concomitant evolution of hydrochloride, ketones and acid chloride moieties. At higher degrees of oxidation, polychloroprene gradually increases in modulus and loses elongation leading to increased hardness and brittleness.

Oxidation initiates at the allylic hydrogen or chlorine atoms; particularly atoms residing in tertiary positions that are formed during 1,2 or 3,4 polymerization (99–101). After an initial induction period, rapid autooxidation increases with temperature (102). At the low monomer conversion characteristic of mercaptan-modified polymers, the concentration of microstructures arising from 1,2 and 3,4 polymerization is lower than that found in higher conversion types. Thus polymers made at low polymerization temperatures with mercaptan modification are the most heat resistant polychloroprene types (103).

Hydrogen chloride evolution with polymer degradation did not occur readily at 120 °C in a nitrogen atmosphere (131). At much higher temperatures (eg, 275 °C), the polychloroprene polymer was carbonized with HCl liberated by a nonfree radical mechanism (104). Polymer polymerized at low temperatures showed better thermal stability (103).

The practical ceiling service temperature in air for conventional polychloroprene polymers used in dynamic applications is approximately 120 °C. To reach this high service temperature, antioxidants, antidegradants are added during rubber compounding. Alternately, theory predicts that elimination of tertiary hydrogens and tertiary chlorine atoms would improve heat resistance. Several studies have supported the theory. Thus, post-reaction of polychloroprene with dodecyl mercaptan (105), use of high levels of ethylene thiourea during curing (106), and inclusion of reactive thios such as mercaptobenzimidazole in the cure systems (107) all react away the labile chlorine atoms thereby improving heat resistance. The latter technique is particularly important in improving the heat resistance of mercaptan-modified polychloroprene.

6. Commercial Conversion of Raw Polymers to Final Vulcanizates

6.1. General Overview. Polychloroprene is a multipurpose elastomer that has a good balance or properties that include outstanding physical toughness and wider short-term/long-term operating temperature range than most general-purpose hydrocarbon elastomers such as EPDM or natural rubber (see Table 3). Polychloroprene has better resistance to hydrocarbon oils, ozone, sun, weather and heat per ASTM D2000/SAE J2000 categories BC/BE. Finally, it demonstrates flame retardency and self-extinguishing characteristics than purely hydrocarbon-based elastomers lack.

As with all elastomers, the properties of the raw polymer can be enhanced by careful choice of rubber compounding formulation (108). Handling precautions, polymer selection guide, compounding guide for specific application, processing guides and representative formularies are discussed in the *Guide to Grades, Compounding and Processing of Neoprene Rubber* compiled initially by J. C. Bament (109). Future mentions of this document will simply be referenced as the Bament guide.

The critical links between the raw polymer and finished vulcanized product used by the global consumer involve the compounding, processing and curing or vulcanization. There are several major considerations in designing a rubber composition based on polychloroprene dry polymers.

1. Selection of a CR or polychloroprene type
2. Choice of a compound formulary for a specific end-use
    a. acid acceptors
    b. vulcanizing agent
    c. vulcanizing accelerators and retarders
    d. antioxidant and antiozonant
    e. re-inforcing and extending fillers

    f. plasticizers
    g. processing aids

3. Modification of the basic formulary to choose critical ingredients necessary to achieve critical end-use properties

6.2. Compounding and Processing of Polychloroprene. Typically, dry polymers are mixed with compounding ingredients on a rotating two-roll mill or Banbury mixer.

Owing to the propensity of the unsaturated polymer to degrade and liberate HCl on long-term in-service use, a special grade of magnesium oxide (Maglite D) from Marine Magnesium Co.) is added as an acid acceptor. As metal oxides can also function as vulcanizing agents, particularly for chloroprene–sulfur copolymers, an optimum level of MgO is used. An antioxidant is required to attenuate the aging process. Antiozonants are added in addition to antioxidants to prevent ozone-induced stress cracking particularly in dynamic applications. Plasticizers and oils enhance the rheological properties and also improve vulcanizate properties. Fillers are of paramount importance for all polychloroprene compounds. Of all fillers, carbon black is most important. Carbon black reinforces the rubber leading to higher tensile strength, greater resistance to oil swell, weather resistance, and abrasion and tear resistance. Plasticizers aid in the mixing of ingredients. Depending on the plasticizers selected, stress-strain properties may be increased or low temperature stiffness resistance improved without affecting crystallization rates. Finally, zinc oxide and accelerators function both as acid acceptors and curatives that initiate the crosslinking reaction. Retarders such as sodium acetate or salicylic acid are used to balance the cure rate or scorch thereby improving curing process safety. In this connection, scorch is defined as cure rate measured on compounded rubber (ASTM D3190-95) as Mooney Scorch with small rotor at 121 °C (ASTM D1646-96A) or MDR scorch measured with a moving die rheometer at 160 °C (ASTM D5289-95).

Curing. Chloroprene–sulfur copolymers can be cured for some applications with zinc oxide alone. All other polychloroprene types will usually require an organic accelerator to cure. Typically thioureas are used in combination with zinc oxide to effect cure. The accepted mechanism for curing involves reaction of thioureas and zinc oxide at the primary allylic chloride moiety that was formed by sn_i' rearrangement during polymerization or curing (111,112).

Thio ureas such as ethylene thiourea initially react with the primary allylic chloride to yield the thio ether. Zinc oxide then react at the thiocarbonyl atom. Further reaction at 160 °C curing temperature eliminates the ethylene urea and leaves the polymer as the zinc sulfide salt. The sulfide salt reacts the allylic chloride moiety of a second polymer molecule to generate the thioether crosslinked polymer (113).

Wide ranges of organic accelerators, which are capable of nucleophilic substitution at the allylic chloride atoms, have been used in polychloroprene curing. Polyhydric phenols (114), hydroxy-phenyl mercapto substituted triazoles (115), thio lactams (116), thiazolidine and thiones, Vulkacite CRV (117), alkyl thioamides, formaldehyde amine reaction products, amines, guanidines, dithiocarbamates, thiurams and sulfenamides have all been used as accelerators.

Antioxidants. The sensitivity of polychloroprene to oxidative attack has been discussed (58,118–120). Antioxidants are required for good long-term service. Amines, hindered phenols and bisphenols are generally the antioxidants of choice. Octylated diphenylamine is frequently used due to its effectiveness, its nonstraining characteristics, and its failure to interfere with the curing reaction (121). Organic monosulfides and phosphates enhance the activity of octylated diphenylamines. *Para*-Phenylene-diamines are used, but are lightly staining antioxidants. Of the bisphenols, 2,2′-methylene-bis-4-methyl-6-*tert*-butyl phenol, 4,4′-thio bis (2-methyl, 6-*tert*-butyl phenol) are important. Neozones (ie, phenyl naphthylamines) are staining antioxidants that have found utility in some applications. When used at levels of 3 to 5 parts per 100 parts rubber, neozones are good antioxidants and good antiozonants (110).

Antiozonants. The reaction of atmospheric ozone with olefins is a known organic chemical reaction. Primary and secondary ozonides are formed (122).

Ozonolysis is most pronounced when vulcanizates are tested under stress-cracking conditions in an atmosphere containing ozone. Owing to the presence of the polar chlorine moieties, polychloroprene resists cracking to a much greater extent than natural rubber or polybutadiene. The long established use of polychloroprene as telephone wire coatings attests to the high ozone resistance of the polymer. Early on, rubber processors considered ozone cracking as a surface phenomenon. Thus waxes that would bloom to the vulcanizate surface were used for ozone protection (123). The use of waxes was, however, not a panacea for all problems involving ozone cracking. W. F. Tully noted as early as 1939 that *p*-phenylenediamines were effective antiozonants (124). The choice of *p*-phenylenediamine was critical, however due to bin instability precipitated by reaction of the bifunctional amine with polychloroprene cure sites leading to increased viscosity (118). The best balance of bin stability and ozone resistance in a dynamic test at 40 °C was achieved by use of a diaryl hindered *p*-phenylenediamine antiozonant.

N-(1,3-dimethyl butyl)-*N*-phenyl-*p*-phenylene-diamine and phenyl/tolyl-*p*-phenylene diamine showed best balance of properties.

Of auxiliary agents, linseed oil, unsaturated vegetable oils, rapeseed oil, and hydrocarbon waxes enhance the efficiency of an antiozonant in a dynamic ozone test as they bloom to the surface of the polymer. Ester plasticizers such as dioctyl sebacate impair ozone resistance presumably due to enhanced solubility of polar esters in the polar polychloroprene network polymer. Finally, the mechanism for ozone attack differs appreciably from oxygen attack at allylic atoms. Thus, an antioxidant is generally used in combination with an antiozonant for polychloroprene.

Plasticizers. Plasticizers are used in polychloroprene to improve compound processability, modify vulcanizate properties, and to reduce cost (see Table 5).

There are five classes of plasticizers normally employed for polychloroprene vulcanization: (*1*) organic esters, (*2*) petroleum oils, (*3*) vegetable oils, (*4*) chlorinated paraffins, (*5*) polymeric plasticizers. Some attributes of the different classes are given in Table 6.

6.3. Processing. *Mixing.* The ability to be mixed in existing equipment used in natural rubber compounding was one factor that contributed to the easy acceptance of polychloroprene after its discovery. Mixing of compounds of various sizes can be performed on two-roll mills or in an internal Banbury mixer.

Several variations of a basic scheme used in the industry are (*1*) upside-down mixing, (*2*) sandwich mixing, (*3*) straight mixing, (*4*) optimum dispersion mixing, and (*5*) masterbatch mixing. Upside down mixing was developed in which all the filler and oil were loaded first into the mixer and then the rubber added on top. The ram lowered and mixing starts. Cold rubber gives more shear on the black at the critical initial stage and therefore a shorter mixing times is obtained with better dispersion. The downside temperature is developed much faster.

The accelerators and zinc oxide are best added on a second mill or in a second operation just before the stock is needed for curing (127). Bin stability is thus enhanced.

Calendering and Extrusion. Friction compounds are used to build up composite structures of fabric and rubber. The surface of the calendered fabric must have good green strength or “building” tack. Thus calendered stocks are usually made from slow crystallizing polychloroprene types. Polychloroprene compounds can be formulated to process well in the four basic calendering operations, which include: unsupported sheet, fractioning, plying-up, and skim coating (128). Unsupported sheet calenders use smooth compounds based on sol/gel blend or “pre-crosslinked” types. These polymers or very low nerve will calender smoothly and rapidly. Plying-up is done when smooth sheets are required in a thickness, which cannot be calendered in one operation. Plying-up gives a better sheet since pinholes and other flaws do not extend through the full thickness of the sheet. Frictioning stocks are very soft and tacky. They permit penetration and adherence to the interstices of the fabric. Slow crystallizing polymers are used for this application. Skim coating is similar to plying-up with the fractioned fabric as one ply.

Extrusion. Polychloroprene has been employed in a wide variety of extrusion processes. Intricate cross-sections such as highway compression seals, bulb weather-stripping, and hose represent a few examples. As with calendering, extrusion is very sensitive to nerve. The DuPont Dow neoprene sol/gel blend types and best suited for extrusion applications. Use of low levels of high structured furnace carbon blacks, stearic acid, petroleum, paraffin wax, triethanolamine benzoic acid and calcium stearate are particularly effective extrusion aids. The screw of the extruder should have a constant diameter root with increasing pitch. Heat history of the compound should be minimized with only a brief warm-up before extrusion begins. The barrel and screw should be run cool, 50 °C, and the die hot, 95 °C (127).

Molding. Molding is used widely for fabricating CR into belts, hose, sponge, and a variety of industrial products. All of the standard molding techniques have been used successfully with commercially available equipment. Molding methods include compression molding, transfer molding, injection molding, blow molding, vacuum molding, and tubing mandrel wrap. An optimum cure cycle-time-temperature relationship must be selected based on the curing characteristics of the compound and the suitability of existing equipment. Mold design must take into consideration the easy rapid removal of the cured part without damage (129). The Bament guide contains specific recommendations on cure condition for specific end-use applications (83).

7. Commercial Polychloroprene Polymers

7.1. General Overview. At one time, 10 worldwide producers manufactured 160 dry polychloroprene types and 66 liquid dispersions or latex types. More recently six major producers produce 93 dry types. The polymers offered globally fall into five categories: (*1*) standard general-purpose grades, (*2*) crystallization resistant grades, (*3*) adhesive grades, (*4*) specialty grades, and (*5*) liquid dispersions or latex grades. The chloroprene–sulfur copolymers, mercaptan-modified homopolymers, and mercaptan-modified sol-gel blend polymers constitute the standard general-purpose grades. Crystallization resistant grades are made by two commercial processes. Copolymerization of chloroprene with 2,3-dichloro-1,3-butadiene is the method adopted by most producers. High temperature and high-pressure emulsion polymerization is a second process used. Adhesive grades are generally made by low temperature polymerizations. The specialty grades are based on xanthogen disulfide chain transfer during either homopolymerization or copolymerization with conventional comonomers or sulfur. Finally, the latex grades are made by the same emulsion polymerization techniques as the dry types but generally with additional surfactants. The latexes are sold as aqueous dispersions. Customers convert the liquid dispersions to dry product according to specific end-uses.

Thus, wide ranges of choices are available for a diverse range of properties.

7.2. Standard Grades. Standard grades are listed in Table 7.

7.3. Global Polychloroprene Grades. The six major global producers manufacture all major classes of commercial polychloroprene dry types (130): DuPont Dow Elastomers L.L.C. manufactures Neoprene, Bayer manufactures Baypren, Enichem makes Butachlor, Denki Kagaku makes Denki chloroprene, Tosoh makes Skyprene and Showa makes Showapren.

Xanthogen disulfide modification has been used in the manufacture of all dry and latex types including chloroprene–sulfur copolymers. The chain-transfer agents have been used in combination with all conventional comonomers. In contrast to dodecylmercaptan modifiers, xanthogen disulfide modification has the advantage that it can be used with chloroprene–sulfur copolymerizations without concerns with reaction with sulfur.

The xanthate-terminated polymers undergo reaction at the end group during vulcanization (131,132). The molecular weight distribution can be wide leading to better processing polymers (103,132). In concert with predictions from the Boltzmann's equation, the reactive ends leads to a polymer of greater tensile strength, reduced hysteresis loss and creep.

The sol/gel blend or "pre-crosslinked grades" of polychloroprene such as the T Type polychloroprenes available from DuPont Dow contain a highly crosslinked network polychloroprene polymer that acts as an internal processing aid (133,134). The blend has many of the same characteristics as the sol component, but different compound rheology properties. This composition results in faster extrusion with extrudates having smoother surfaces. Extrudates also retain their shape better with good definition until vulcanized.

8. Commercial Dry Type Applications

The *Guide to Grades, Compounding and Processing of Neoprene Rubber* compiled initially by J. C. Bament lists the major dry type applications and starting formularies for compounds to meet the specific end uses (109).

Formularies for the following applications are included: adhesives; automotive; bridge bearing pads; cable jackets; cellular products; coated fabrics; conveyor belts; footwear; hose; power transmission belts; profiles; roll covers; sheeting; and tank lining.

9. Latex or Liquid Dispersions

9.1. General Overview. Polychloroprene latexes are aqueous dispersions of synthetic polychloroprene polymers with surfactants. The surfactants of choice are markedly different than the protein-based surfactants contained in natural rubber latex that is reportedly at the root of human hypoallergenic reactions associated with the use of natural rubber latex.

Latex products are manufactured in the identical fashion as the dry polymers described earlier. One major exception is that the primary and auxiliary surfactants used in latex manufacture are not destroyed prior to shipment to the end-user. Molecular weight control is identical with mercaptan, organic halides, and xanthogen disulfides chain transfer agents being typically used. Copolymerizations are conducted with the same variety of co-monomers that include 2,3-dichloro-1,3-butadiene, sulfur, and acrylic acids and esters. Polymerization temperatures are varied from 5 to 50 °C at atmospheric pressures to control polymer microstructure and crystallinity. The choice of surfactant package for latex products is much more critical than for dry types, since the latex must remain colloidally stable for time-period measured in weeks or months instead of hours as required in dry type manufacture.

Since the latexes contain discrete stabilized polymer particles that are dispersed in the aqueous medium, the latex displays good rheological properties. The latex polymer structures can differ appreciably from dry types. Long-chain branching and gelled structures are more tolerable in latex, since the polymer does not need to be isolated by freeze roll. The branched and gelled structures offer advantages to the end-users who fabricate adhesives having high cohesive strength, high stress-strain characteristics and high bond strength at elevated temperatures (Fig. 4).

Low temperature polymerization yields crystalline polymers having high room temperature bond strength, high cohesive strength and good stress-strain characteristics (Fig. 5).

The two phenomenon form the basis for propagating the global adhesive product line of which the following is indicative.

9.2. Global Latex Product Line. There are three general classes of polychloroprene latexes: anionic, cationic and nonionic. By far, the anionic latex class constitutes the largest commercial volumes for general use. Cationic latexes are usually made with quaternary ammonium salts and are made in the smallest volume types. The nonionic latexes differ appreciably from ionic lattices in several important aspects of which chemical and mechanical stability is the major differences (see Table 8).

9.3. The Theoretical Basis of Latex Stabilization. The colloidal stability of each class of latex is primarily dependent on the effectiveness of the surfactant. In the high permittivity of water, most polymer colloid particles carry an electric charge. These electric charges arise from the ionization of groups at the polymer surface. In ionic polychloroprene emulsions, the electric charges are formed by the neutralization of substituted carboxylated diterpenes (rosins and resins) with caustic during the emulsification process.

The surface of the polymer particle is smooth and charges are uniformly distributed over the surface. To satisfy the condition of electroneutrality, the sodium carboxylate moiety resides at the interphase with sodium counterions solubilized in the aqueous phase near the carboxylate coions. The spatial distribution of coions and counterions form the electronic "double layer" of $1/\kappa$ thickness. This boundary layer stabilizes the colloid (136). In the 1940s Derjagin, Landau, Verway, and Overbeek suggested that the electrostatic stability (86) of latexes could be explained on the basis of three potential energy terms that include repulsive potential energy (V_R), Van der Waal attraction (V_A) and the Born potential (V_B). This theory became widely known as the DLVO theory.

$$V_{\text{total}} = V_R + V_A + V_B$$

Latex stability is achieved when the electrostatic repulsion term, V_R, dominates attractive forces at the inter-particle distance near $4/\kappa$. At very close interparticle distances, a potential energy barrier is encountered. If particles are forced over the potential energy barrier to the primary minimum, permanent coagulation occurs (Fig. 6).

Thus, stability is heavily dependent on repulsive energies which are functions of at least three variables: boundary layer thickness; valence of the counterion and ionic contaminants; and concentrations of electrolyte. As electrolyte concentration is increased, the electronic double layer thickness decreases, the particles move toward the primary maximum and coagulation occurs. Multivalent counterions are important adjuvant for dipped goods manufacture where chemical coagulation is required.

In the latex end-use applications, DLVO stabilization must be considered in designing a latex compound.

9.4. Latex Compounding. Polychloroprene latexes are used in six general applications: adhesives, binders, coatings, dipped goods, elasticizers, and foam. The conversion of the raw latex to a tough finished product depends on compounding and curing. Latex compounding has one complication not present for dry types. The colloid chemical and mechanical stabilities of the aqueous dispersion containing added compounding ingredients must be considered. Masterbatching vs individual dispersion make-up will minimize introduction of electrolytes, facilitate dispersion of difficult materials, minimize processing mistakes, lower cost, increase production rates, and generally generate less waste. Mechanical stability during compounding is enhanced by control of seven variables: Use of

1. tanks and pipes having smooth interiors;
2. low shear and low speed agitators with no dead spots;
3. gravity flow where possible;
4. positive displacement pumps—no gear or pinch pumps; where gravity flow is not possible
5. air pressure only to transfer but not to store latex;
6. areas of high humidity to decrease evaporation rates; and
7. filtration of the compound if viscosity permits.

Compounding Ingredients. Depending on the application, a latex compound may contain up to nine compounding ingredients: deionized water, antifoam, colloidal stabilizers, polymer stabilizers, curatives, tackifiers, fillers, and thickeners. All have specific functions that contribute to the outcome of the finished part.

The latex can be chosen from a wide variety of liquid dispersions available based on the crystallization and gel properties desired (137,138).

Antifoam. It is best to prevent foam from forming in the latex than to eliminate foam by use of defoamer. To prevent foam formation, avoid free fall of latex or any dispersion and emulsion, which contain surfactants that will facilitate foam formation. When mixing latex with other ingredients, the agitator impeller should be turned off until the blade is covered with latex. Any fillers, which may have absorbed air on the particles, should be pre-wetted and foam allowed to subside before adding the fillers to the latex compound.

Colloidal Stabilizers. Colloidal stabilizers are normally added to increase shear stability of anionic latexes, improve chemical stability of nonionic latexes and to sequester cations. The surfactants are also used to wet water insoluble additives. Anionic stabilizers such as potassium resinates, potassium caseinate or Darvan WAQ are used with anionic latexes to improve the mechanical stability in coating and binders. Darvan SMO, sodium sulfated methyloleate, is specifically recommended for use in dipping compounds to improve smoothness and to eliminate striations. Tritons, Igepals, Tergitols are added to nonionic latexes to improve chemical stability. Cationic latexes require cationic or nonionic surfactants (Darvan NS). Cations are normally sequestered with Calgon, sodium silicate or trisodium phosphate.

Polymer Stabilizers or Antioxidants. No polychloroprene latex compound is complete without additives that give adequate protection against polymer oxidation. The oxidation studies for dry types also apply to polymers contained in latexes. Hindered phenols are used in many applications. When used at 1-phr, Wingstay L (butyrated-*p*-cresol-bicyclopentadiene) provides adequate protection in most adhesive applications. The bisphenols are nonstaining and generally nondiscoloring.

Curatives. Consistent with dry type technology, metal oxides have three functions in a latex compound. Zinc oxide participates in the curing reaction and is an effective acid scavenger. In application where the substrate is not acidic, zinc oxide is not needed. Such substrates include chrysoltile asbestos gaskets or the hydraulic cement in elasticized concrete.

Sulfur is occasionally added to polychloroprene latexes to achieve a higher state of cure. Added sulfur is not effective for chloroprene-sulfur copolymer latexes. Films containing 1-phr sulfur darken considerably upon curing. Retention of elasticity of such films decreases further on continued exposure to heat.

Accelerators. Accelerators catalyze the cross-linking of the polymers by a similar mechanism described for dry types. The latex version has some advantage over dry types in that many of the crosslinks for latex types were formed during polymerization. The use of thiocarbanilide (*N*,*N*′-thiourea) yields products of higher modulus; lower tensile strength and best oil swell resistance. Butyl Zimate (zinc dibutyl dithiocarbamate) is practically equivalent to thiocarbanilide cures but imparts less color change. Tepidone (sodium dibutyl dithiocarbamate) and tetraethyl thiuram disulfide (TETD) give products of lower modulus, higher tensile strength, higher elongation, and less color.

Ultraviolet Ray Screeners. Carbon black and red iron oxide provide additional resistance to degradation from exposure to sunlight. They are used only sparingly, however, due to discoloration at the adhesive line.

Fillers. Fillers are used in compounds to increase viscosity, increase solids, and to lower cost. Most fillers used in latex do not exhibit the reinforcing effect that is characteristic of their use in dry type polychloroprene. Water-washed whiting (calcium carbonate) can be added directly to the latex. Most clays are acid and must be neutralized and slurred before adding to the latex. When used at levels ranging from 10 to 20-phr, fine clays such as DIXIE Clay can add some degree of reinforcement. Hard clays have much smaller particle size than soft clays. Feldspar can be added directly to the latex but will tend to settle quickly. Hydrated alumina is used primarily to improve flame retardency and to, improve water resistance. Large particle size hydrated alumina can be added directly to the latex.

Thickeners. Thickeners are always the last ingredients to be added. Polyacrylates are the preferred thickeners for polychloroprene latex. They are usually diluted with equal parts of water to generate a pourable fluid, which can be added directly to the compound. Algums have higher viscosity stability than polyacrylates at high pH. Cellulose derivatives are effective thickeners but are much more difficult to handle, usually requiring back mixing with a small amount of latex before adding it to the compound. Bentonite clay is a favorite thickener for very high viscosity adhesives such as mastics. Fumed silica is a good choice for latex formulations having a pH of 7–10.

Biocides. Waterborne systems of less than 10-pH are prone to bacterial attack. The phenomenon is normally not a problem with solvent-borne systems. Bacterial infestation normally manifests itself by malodor, discoloration, and gas evolution. Nuosept 95 is an effective biocide.

9.5. Latex Applications. A good way to remember the applications for latex is to follow the first six letters of the alphabet. A = adhesives, B = binders, C = coatings, D = dipped Goods, E = elasticizers, and F = foam.

Adhesives. An adhesive is a continuous film sandwiched between two substrates. Polychloroprene latexes are used as waterborne contact bond adhesives where a latex-based adhesive compound is placed on both substrates to be bonded. Immediately before the two coated surfaces dry, the two substrates are placed together and bonded. Many of the environmental, personnel exposure, and potential fire hazards associated with the use of aromatic-hydrocarbon-solvent adhesives are avoided by the use of latex adhesives. Both anionic and nonionic latexes are used in adhesive applications. The high-uncured strength, high cohesive strength, high internal strength and good contactibility of polychloroprene with a variety of substrates are attributes that make polychloroprene useful in this application. The high-uncured strength of the adhesive arises from the crosslinks made in the latex during polymerization.

Binders. A binder is a mixture of discrete polymer particles distributed throughout a matrix. The particulates can be cellulosic, ground leather, or ground rubber. The high internal bond strength of polychloroprene makes the latexes useful for binding cellulosic fibers in sandpaper. Up to 17×10^6 pounds/year of polychloroprene latex have been used for shoeboard applications. Regenerated leather made by use of polychloroprene latex to bind ground leather scraps is a prominent example of use as a binder. Wet-web saturation with polychloroprene is used in shoeboard applications requiring a flexible polymer of high binder efficiency, adhesive solvent resistance, moisture and chemical resistance. The high durability, resistance to weather and resilience without curing are polychloroprene properties that find utility in fabrication of resilient surfaces such as tennis courts and athletic tracks.

Coatings. Coatings are continuous films adhering to one substrate. The substrate can be fiberglass, fiberglass bats, fabrics, composite laminates, or carpet. Polychloroprene has been used in all of these applications due to its erosion resistance, chemical resistance, abrasion resistance, weather resistance, sound dampening characteristics, thermal insulation properties and the inability of properly formulated polychloroprene to support combustion. Fiberglass and fiberglass bats used in construction ducts are coated with polychloroprene latex to prevent fiberglass particles from contaminating air that passes through the ducts. Polychloroprene-coated fiberglass provides good thermal insulation and sound dampening. Polychloroprene-coated fiberglass is used under automotive hoods to provide a degree of flame retardency and sound dampening.

Woven fabrics used for printer blankets are coated with polychloroprene to provide resistance to solvent and inks. Polychloroprene composite laminates for industrial suits (eg, fire-fighter's suits) are coated with polychloroprene to provide chemical resistance, weather/abrasion resistance, durability and a degree of flame retardency.

Rugs and upholstery can be coated with polychloroprene latex; particularly those used in aircraft. Flame retardency is a key property highlighted.

There are advantages and disadvantages to using polychloroprene latexes in these applications. The gelled polymer from polymerization provides high uncured strength; particularly in applications where post curing is not practical. The disadvantage lies in the high pound/volume cost. Thus, latexes that permit high filler loading to reduce cost without much sacrifice of properties are successful in these applications.

Dipped Goods. Dipped goods are continuous films (supported or unsupported) that are usually formed by chemical coagulation of latex compounds. Polychloroprene latexes are used in a variety of dipped goods applications that include automotive, tractor shift controls, convoluted parts, windshield wiper blades, supported and unsupported gloves, and meteorological balloons. The major advantages of polychloroprene are ozone resistance in objects having sharp contours, durability, chemical resistance, flexibility, feel, tear strength, oil/chemical/abrasion resistance and resistance to ultraviolet rays. Generally the latexes are sold to a latex compounder who formulates the latex for the end-use fabricators. Polychloroprene latexes have many advantages over natural rubber in terms of resistance to household and industrial detergents and chemicals. Gloves made from polychloroprene have 100% chemical resistance, oil resistance, ozone resistance, and heat resistance.

A unique application involves meteorological balloons. Balloons made from polychloroprene are used to convey sensors up to 150,000 feet into the atmosphere for purposes of determining the direction of weather currents. A special combination of stress-strain properties, resistance to ozone, and ultraviolet sunrays are important for optimum functioning of the balloon.

Elasticizers. Elasticizers are composites of small particles of near molecular size that are distributed throughout some medium. Latexes are formulated into elasticized concrete to minimize stress cracking that is precipitated by concrete expansion and contraction. The application is extremely important for decks on ships, decks in high-rise garages, hospital floors, kitchens, and gym floors. Latex-modified concrete provide vibration dampening in the workplace that reduce fatigue to personnel (eg, operating rooms) who need to stand for extended periods of time while working.

Latex modified asphalt and bitumen represent other elasticizers. Latex modification not only reduces stress cracking but also provides adhesion for rocks and chip asphalt fillers. The adhesion prevents chips from flying out of the asphalt on highways and breaking windshields. Many states in the United States require latex modified asphalt in road construction. All classes of latexes can be used in concrete and asphalt modification.

Foam. Foam is a continuous open-celled matrix produced from froth or coagulation onto a pre-formed cellular matrix. Over the years, polychloroprene latexes have been used in nursing homes, in mattresses, in journal boxes, in sea-going vessels, in cushioning and in seating. Properly formulated froth and parts made from polychloroprene latexes are water resistant and have a high degree of flame retardency. The journal box application for locomotive lubricants depends on the oil resistance of polychloroprene to deliver oil from the reservoir to the axle of the train. Polychloroprene suffers from two major disadvantages in foam applications: costs and weight. Both limit full utility of these foams in aircraft applications.

Two processes have been used to make foams from froth. For thin foams, dry coagulation is an effective procedure. For thicker foams, chemical coagulation, chemical gel and heat gellation are used.

10. Economic Aspects

The United States producer of polychloroprene is DuPont Dow. The 2001 capacity of their Laplace, La. plant was 46×10^3 t and the capacity of their Louisville, Ky. plant was 90×10^3 t.

Demand for polychloroprene has declined about 3%/yr for the period 1996–2001. This is mainly because of its relatively high price and increasing substitution from competing elastomers. This trend is most notable in the automotive sector.

Polychloroprene's strengths are its high resilience and excellent resistance to ozone, flames, and weathering. It also possesses high strength and good resistance to a wide variety of coated fabrics. Substitution in these markets is believed to have run its course (139). Demand in 2001 was 55×10^3 t. The projected demand for 2005 is 51×10^3 t.

Price history for the period 1996–2001 was a high of \$1.95–3.04/lb and a low of \$1.81–2.18/lb.

11. Quality Management

For major polychloroprene producers the quality management systems are described by the international ISO9001-2000 protocol.

12. Health and Safety Factors

Since chloroprene and dichlorobutadiene monomer will undergo runaway reaction, the successful producers of polychloroprene polymers have learned how to safely handle the hazardous monomers and monomer intermediates in large-scale quantities. Monomer synthesis and storages represent the largest concentration of monomers during commercial manufacture. Polymerization, albeit in aqueous media, present safety challenges due to presence of free radical.

Prevention of runaway reactions involving these highly reactive monomers involve strict adherence to six fundamental principles for monomer handling: Keeping it cold, keeping it free of air and oxygen by storage in a nitrogen atmosphere, keeping it inhibited where possible, keeping it moving, keeping it free of contaminants such as popcorn polymer and iron, and keeping it diluted where possible.

Residual monomer remaining after polymerization pose a lesser degree of hazard due to low concentration and engineering measures implemented in the workplace to prevent personnel exposure to the monomer. Neoprene liquid dispersions contain less than 0.1% residual chloroprene monomer.

The amount of excess caustic in neoprene polychloroprene liquid dispersions is approximately 0.1%. The liquid dispersions are, however, very basic having pH near 12. While not corrosive in animal tests, eye protection and skin protection are essential in areas where personnel exposures are possible due to possible irritation.

Some dry polychloroprene types have been shown to have low oral toxicity in rates. Human patch test for several dry types showed no skin reactions (140). The FDA status of neoprene polychloroprene is described in the literature (141).

BIBLIOGRAPHY

"Elastomers, Synthetic – Neoprene" in *ECT* 3rd ed., Vol. 8, p. 515–535, by R. R. Johnson, E. I. du Pont de Nemours & Co., Inc.; "Elastomers, Synthetic, Polychloroprene" in *ECT* 4th ed., Vol. 8, pp. 1045–1079, by W. K. Witsiepe, E. I. du Pont de Nemours & Co., Inc.

1. W. R. Remington and J. S. Lann, JLR-29-5, No. 26.
2. P. A. Lovell and M. S. El-Aasser, *Emulsion Polymerization and Emulsion Polymers*, John Wiley & Sons, Inc., New York, p. 28.
3. L. J. Op, P. J. Hwan, and B. H. On, *Hwahak Kwa Hwahak Kongop* **20**, 119 (1977).
4. W. Kern and co-workers, *Macromol. Chem.* **3**, 223–246 (1950).
5. C. A. Stewart, Jr., *Am. Chem. Soc.* **93**, 4815 (1971); **94**, 635 (1972).
6. F. Hrabak and J. Webr, *J. Macromol Chem.* **104**, 275 (1967).
7. I. Williams, *Ind. Eng. Chem.* **31**, 1204 (1939).
8. S. Ekegren and co-workers, *Acta Chem. Scand.* **4**, 126 (1950).
9. K. A. Nersesyan, R. O. Chaltykyan, and N. M. Beileryan, *Arm. Khim. Zh.* **40**(2), 92–95 (1987).
10. R. N. Haward, *J. Polym. Sci.* **4**, 273, 1949.
11. U.S. Pat. 3,925,294 (1975), A. M. Doyle (to E. I. du Pont de Nemours & Co., Inc.).
12. D. H. Napper, *Polymeric Stabilization of Colloidal Dispersions*, Academic Press, New York, 1983, p. 41.
13. Ref. 12, p. 38.
14. Ref. 12, p. 667.
15. R. C. Ferguson, *J. Polym. Sci, Part A2*, 4735 (1964).
16. P. A. Lovell, T. H. Shah, and F. Heatley, *Polym. Communication* **32**, 98–103 (1991).
17. R. G. Gilbert, *Emulsion Polymerization A Mechanistic Approach*, Academic Press, New York, pp. 189–190.
18. W. E. Mochel, *J. Amer. Chem. Soc.* **71**, 1426 (1949).
19. Fr. Demand FP 2,556,730 (June 21, 1985), P. Branlard and F. Sauterey (to Distugil SA).
20. H. G. Elias, *Macaromolecules, Structure and Properties*, Plenum, New York, 1977.
21. M. Buback and co-workers, *J. Polym Sci., Letters Ed.* **26**, 293 (1988).
22. R. A. Hutchinson, M. T. Aronson, and J. R. Richards, *Macromolecules* **26**, 6410–6415 (1993).
23. Ref. 12, p. 28.
24. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience Publishers, New York, 1988, p. 522.
25. Eur. Pat. Appl. EP 146,131 (June 26, 1985), N. Emura, T. Ariyoshi, and T. Kato (to Toyo Soda Mfg. Co., Ltd.).
26. Jpn. Kokai Tokkyo Koho JP 61,238,808 (Oct. 24, 1986), M. Kamezawa, T. Ariyoshi, and Y. Sakanaka (to Toyo Soda Mfg. Co., Ltd.).
27. Y. Miyata and M. Sawoda, *Polymer* **29**, 1495 (1988).
28. Ger. Offen. DE 3,344,065 (June 7, 1984), E. M. Banta and K. D. Fitzgerald (to Denka Chemical Corp.).
29. Jpn. Kokai Tokkyo Koho JP 59 056,440 (Mar. 31, 1984), (to Toyo Soda Mfg. Co., Ltd.).

30. Jpn. Kokai Tokkyo Koho JP 61 118,440 (June 5, 1986), Kato and co-workers, (to Toyo Soda Co., Ltd.).
31. Eur. Pat. Appl. EP 421,149 (Apr. 10, 1991) S. Ozoe and H. Yamakawa (to Tosoh Corp.).
32. L. J. Op, P. J. Hwan, and B. H. On, *Hwahak Kwa Hwahak Kongop* **20**(6), 299 (1977).
33. H. K. Banock, R. S. Lehrle, and J. C. Robb, *J. Polym. Sci., Part C* **4**, 1165 (1964).
34. G. H. Miller, G. P. Chock, and E. P. Chock, *J. Polym. Sci., Part A* **3**, 3353 (1965).
35. A. N. Pravednikov and S. S. Medvedev, *Dokl. Akad. Nauk., USSR* **109**, 579 (1956).
36. M. F. Margantova and M. P. Zverev, *Ukr. Khim. Zh.* **23**, 734 (1957).
37. U.S. Pat. 2,942,037 and 2,942,038 (June 21, 1960), P. A. Jenkins (to Distillers Co., Ltd.).
38. U.S. Pat. 2,770,657 (Nov. 13, 1956), J. R. Hively (to E. I. du Pont de Nemours & Co., Inc.).
39. U.S. Pat. 3,175,012 (Mar. 23, 1965), G. P. Colbert (to E. I. du Pont de Nemours & Co., Inc.).
40. C. A. Aufdermarsh, *J. Org. Chem.* **29**, 194 (1964); C. A. Aufdermarsh and R. Pariser, *J. Polym. Sci.* **A2**, 4727 (1964); R. C. Ferguson, *J. Polym. Sci.* **A2**, 3969 (1966).
41. N. G. Gaylord and co-workers, *J. Polym. Sci.* **A2**, 3969 (1966).
42. N. G. Gaylord and co-workers, *J. Polym. Sci. A-1* **4**, 2493 (1966).
43. N. G. Gaylord and co-workers, *J. Amer. Chem. Soc.* **85**, 641 (1963).
44. U.S. Pat. 3,004,011 (Feb. 5, 1958), H. L. Jackson (to E. I. du Pont de Nemours & Co., Inc.); U.S. Pat. 3,004,012 (Feb. 5, 1958), K. L. Seligman and H. L. Jackson (to E. I. du Pont de Nemours & Co., Inc.).
45. N. G. Gaylord and B. K. Patnik, *J. Polym. Sci.* **13**, 837 (1975); A. Masaki, M. Yasui, and I. Yamashita, *J. Macromol. Sci.-Chem.* **A6**, 1285 (1972).
46. T. Okada and M. Oysuru, *J. Appl. Polym. Sci.* **23**, 2215 (1979).
47. K. Irako and co-workers, *Nippon Kagaku Kaishi*, (4), 670 (1967); K. Irako, H. Koyama, and A. Shisra, *Kogyo Kagaku Zasshi* **74**(10), 2210 (1971).
48. X. Han, F. Guo, and D. Wang, *Yingyong Huaxue* **1**(3), 41 (1984).
49. X. Han and E. Chen, *Gaofenzi Tongxum*, (6), 435 j (1985).
50. J. P. Kennedy and S. C. Guhaniyogi, *J. Macromol. Sci., Chem.* **A18**(1), 103 (1982).
51. M. M. Coleman, D. L. Tabb, and E. G. Brame, *Rubber Chem. Technol.* **51**, 49 (1978); M. M. Coleman and E. G. Brame, *Rubber Chem. Technol.* **51**, 668 (1978).
52. R. J. Petcavich and M. M. Coleman, *J. Macromol. Sci.-Phys.* **B18**, 47–71 (1980).
53. J. R. Ebdon, *Polymer* **15**, 782 (1974); D. J. T. Hill, J. H. O'Donnell, and P. W. O'Sullivan, *Polymer* **25**, 569 (1984); A. A. Kahn and E. G. Brame, Jr., *Rubber Chem. Technol.* **50**, 272 (1977).
54. R. E. Cais and G. J. Stuk, *Macromolecules* **13**, 415 (1980).
55. F. Riva, A. Porte, and C. D. Monica, *Colloid Polym. Sci.* **259**, 606 (1981); C. Della Monica and co-workers, *Conv. Ital. Sci. Macromol. [Atti]* **2**(6) 179 (1983); A. Forte and co-workers, *Conv. Ital. Sci. Macromol. [Atti]* (5), 381.
56. R. Petiaud and Q. R. Pham, *J. Polym. Sci. Polym. Ed.* **23**, 1333–1334 (1985).
57. J. Brandrup and E. H. Immergut, eds., *Polymer Handbook*, 3rd ed., John Wiley & Sons, Inc., New York, 1989.
58. H. C. Bailey, *Revue Generale du Caoutchou Plastique*, **44**(12), 1495–1502, (1967).
59. R. R. Garrett, C. A. Hargraves, and D. V. Robinson, *J. Macromol. Sci. Chem A4*, 1679 (1970).
60. T. A. Babushkina, L. N. Gvozdeva, and G. K. Semin, *J. Mol. Struct.* **73**, 215 (1981).
61. T. A. Babushkina and co-workers, *Vysokomol. Soedin. Ser. A* **23**(8), 1810 (1981).
62. R. Petiaud and Q. T. Pham, *J. Polym. Sci., Polym. Chem. Ed. 23*, 1343 (1985).
63. M. M. Coleman and co-workers, *J. Polym. Sci. Polym. Letters Ed.* **12**, 577 (1974); D. L. Tabb, J. L. Koenig, and M. M. Coleman, *J. Polym. Sci. Phys. Ed* **13**, 1145 (1975).

64. M. M. Coleman, P. C. Painter, and J. L. Koenig, *J. Raman Spect.* **5**, 417 (1976); M. M. Coleman, R. J. Petacvich, and P. C. Painter, *Polymer* **19**, 1243 (1978).
65. T. T. Okaya, T. Tanaka and K. Yuki, *J. Applied Polym. Sci.*, **50**, 745 (1993)
66. G. V. Schulz and L. Roberts-Nowakowsha, *Makromol. Chem.* **80**, 36 (1964).
67. D. Stein, *Makromol. Chem.* **76**, 170 (1964).
68. F. R. Mayo, *J. Amer. Chem. Soc.* **65**, 2324 (1943).
69. W. E. Mochel, *J. Polym. Sci.* **8**, 583 (1949).
70. R. C. Jordan and M. L. McConnell, *ACS Symposium Ser.* **138**, 107 (1980).
71. H. Lange, *Colloid Polym. Sci* **264**(6), 488–493 (1986).
72. P. A. Lovell, T. H. Shah, and F. Heatley, Correlation of the Extent of Chain Branching with Reactor Conditions for Emulsion Polymerization of *n*-Butyl Acrylate in E. S. Daniels, E. D. Sudol, and M. El Asser, eds., ACS Symposium Series, k, Polymer Latexes-Preparation, Characterization and Applications (ACS, Washington D.C.), vol. 492, pp. 188–202.
73. H. Mark, *Der feste Korper*, Hirzel, Leipzig, 1938, p. 103; F. Rodriguez, *Principles of Polymer Systems*, Hemisphere Publishing Corporation, New York, 1989, p. 185.
74. E. E. Drott and R. A. Mendelson, *J. Polym. Sci., A-2* **8**, 1361 (1970).
75. G. Kraus and C. J. Stacy, *J. Polym. Sci., Polym. Phys. Ed.* **10**, 657 (1972); *J. Polym. Sci. Polym. Symp.* **43**, 329 (1973).
76. M. M. Coleman and R. E. Fuller, *Macromol. Sci., Phys.* **11**(3), 419 (1975).
77. Ger. Offen. DE 3,105,339 (Feb. 13, 1981), U. Eisele and co-workers (to Bayer AG).
78. U.S. Pat. 2,914,497 (Nov. 24, 1959), W. J. Keller (to E. I. du Pont de Nemours & Co., Inc.).
79. Eur. Pat. Appl. EP 426,023 (May 8, 1991), F. Y. Kafka, A. R. Bice, and D. K. Burchett (to E. I. du Pont de Nemours & Co., Inc.).
80. Jpn. Kokai Tokkyo Koho JP 58,180,501 (Oct. 22, 1983), (to Kenki Kagaku Kogyo); Jpn. Kokai Tokkyo Koho JP 58,189,202 (Nov. 4, 1983), (to Denki Kagaku Kogyo).
81. *Toyo Soda Kenkya Hokoku* **26**(2), 93 (1982).
82. *Toyo Soda Kenkyu Hokoku* **24**, 83 (1979).
83. P. R. Johnson, *Rubber Chem. Technol.* **49**, 650–702 (1976).
84. U.S. Pat. 2,264,173 (Nov. 25, 1941), A. M. Collins (to E. I. du Pont de Nemours & Co., Inc.).
85. C. A. Hargreaves II in J. P. Kennedy and E. G. Tornqvist, eds., *Polymer Chemistry of Synthetic Elastomers*, Wiley-Interscience, New York, 1968, pp. 227–252.
86. D. V. Derjagin and L. Landau, *Acta Physicochim, USSR* **14**, 633 (1941); E. J. W. Verway and J. Th. G. Overbeek, *Theory of Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.
87. R. S. Barrows and G. W. Scott, *Ind. Eng. Chem.* **40**, 2193 (1948).
88. G. E. Alves, *Chem. Eng. Progr.*, **66**(7), 50–67 (1970).
89. U.S. Pat. 2,831,842 (Apr. 22, 1958), C. E. Aho (to E. I. du Pont de Neumours & Co., Inc.).
90. L. M. White and co-workers, *Ind. Eng. Chem.* **37**, 770 (1943).
91. W. R. Krigbaum and R. J. Roe, *J. Polym. Sci., Part A* **2**, 4391 (1964); W. R. Krigbaum, Y. I. Bata, and G. H. Via, *Polymer* **7**, 61 (1966); A. K. Bhowmick and A. K. Gent, *Rubber Chem. Technol.* **56**, 845 (1983).
92. R. M. Murray and J. D. Detenber, *Rubber Chem. Technol* **34**, 668 (1961).
93. J. T. Maynard and W. E. Mochel, *Polym. Sci.* **13**, 242 (1954).
94. G. I. Tsereteli, I. V. Sochava, and A. Buka, *Vesta Leningr. Univ., Fiz. Khim.* **1975**, 67 (1975).
95. M. M. Coleman, R. J. Petcavich, and P. C. Painter, *Polymer* **19**, 1253 (1978).
96. B. Y. Teitelbaum and N. P. Anoshina, *Vysokol. Soedin.* **7**, 978 (1965); B. Y. Teitlebaum and co-workers, *Dokl. USSR Phys. Chem. Sec., (English)* **150**, 463 (1963).

97. C. W. Bunn, *Proc. R. Soc. London, Ser. A.* **180**, 40 (1942).
98. A. S. Kuzminskii and R. Ya *Peschanskaya, Dokl. Akad. Nauk. SSSR* **85**, 1317 (1952).
99. R. J. Petcavich, P. C. Painter, and M. M. Coleman, *Polymer* **19**, 1249 (1978).
100. V. S. Davtyan and co-workers, *Arm. Khin. Zh.* **42**, 7 (1989).
101. K. Itoyama and S. Mastunaga, Preprints of the ACS 122nd Rubber Division Meeting, Chicago, Oct. 4, 1982, American Chemical Society, Washington, D. C.
102. H. C. Bailey, *Rev. Gen Caoutch. Plast.* **44**, 1495 (1971).
103. U.S. Pat. 3,988,506 (Oct 26, 1976), M. Dohi, T. Sumida, and K. Yokobori (to Denki Kagaku Kabushiki); Eur. Pat. Appl. EP 223,149 (May 27, 1987), T. Takeshita (to E. I. du Pont de Nemours & Co., Inc.); Eur. Pat Appl. EP 175,245 (Mar. 26, 1986), T. Takeshita (to E.I. du Pont de Nemours & Co., Inc.).
104. D. L. Gardner and I. C. McNeill, *Eur. Polym. J.* **7**, 569, 593, 603 (1971).
105. K. L. Seligman and P. A. Roussel, *Rubber Chem. Technol.* **34**, 869 (1961).
106. T. E. Schroer, *Approaches to Improved Heat Resistance for DynamicApplications*, Du Pont Elastomers Bulletin C-NP-510.0584, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. 1984.
107. *The Synthetic Rubber Manual*, 11th ed., Int. Institute of Synthetic Rubber Producers, Inc. Houston, Tex., 1989.
108. P. K. Freakley and A. R. Payne, *Theory and Practice of Engineering with Rubber*, Applied Science Publishers, Ltd., London, 1978.
109. L. Outzs, ed., *Neoprene Polychloroprene. A Guide to Grades Compounding & Processing of Neoprene Rubber*, du Pont Dow Elastomers (2002) original Guide was compiled by J. C. Bament of E. I. du Pont de Nemours and is currently known as the "Bament Guide".
110. N. L. Catton, *The Neoprenes*, The Rubber Chemical Division, E. I. du Pont de Nemours & Co., Inc., 1953, p. 5.
111. N. Kawasaki and T. Hashimoto, *J. Polym. Sci. Polym. Chem. Ed.* **11**, 671 (1973).
112. Y. Miyata and M. Atsumi, *Rubber Chem. Technol.* **62**, 1 (1989).
113. R. Pariser, *Kunstst.* **50**, 623 (1960).
114. H. Kato and H. Fujita, *Rubber Chem. Technol.* **55**, 949 (1981); Jpn. Kokai Tokkyo Koho JP 02,28,532 (Dec. 10, 1990) N. Yamamoto and co-workers (to Ouchi Shinko Chem. Ind. Co., Ltd.); N. Yamamoto and co-workers, *Nippon Gomu Kyokaishi* **64**, 48 (1991).
115. W. Schunk and co-workers, *Gummi, Fasern, Kunstst.* **43**, 617 (1990); F. M. Helay and co-workers, *Elastomerics* **121**(9), 26 (1989).
116. Y. Sakuramoto and co-workers, *Nippon Gomu Kyokaishi* **56**(4), 218 (1983).
117. U. Eholzer and T. Kempermann, *Rubber Plast News*, 49 (May 25, 1981); W. Warrach and D. Tsou, *Elastomerics* **116**, 26 (1984).
118. W. Schmidt, *Curing Systems for Neoprene*, Du Pont Bulletin NP-330.1, 1982; J. C. Bament, *Neoprene Compounding and Procesing Guide Plus Formulary*, E. I. du Pont de Nemours & Co., Inc., 1987; R. M. Murray and D. C. Thompson, The Neoprenes, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1963.
119. R. M. Murray and D. C. Thompson, *The Neoprenes*, E. I. du Pont de Nemours & C., Inc., Wilmington, Del., 1963.
120. Fr. Demande FR 2,459,266 (Jan 9, 1981) J. E. Vostovich (to General Electric Co.).
121. D. C. H. Brown and J. Thompson, *Rubber World* **185**(2), 32–35 (1981).
122. P. S. Bailey, *Ozonization in Organic Chemistry*, Vol. 1, Academic Press, New York, 1978.
123. B. S. Biggs, *Rubber Chem. Technol.* **31**, 1015 (1958).
124. W. F. Tully, *Ind. Eng. Chem.* **31**, 714 (1939).
125. E. Ronde, H. Bechen, and M. Metzger, *Kautsch. Gummi, Kunstst.* **42**, 1121 (1989); E. Ronde. H. Bechen, and M. Mezger, *Polychloroprene Grades and Compounding for*

Long Term Flexibility at Low Environmental Temperatures, Scandinavian Rubber Conference SCR/1989, Tampere, Finland, Jan. 30, 1989.

126. *UK Res Discl.* **211**, 403 (Du Pont (UK) Ltd.).
127. S. W. Schmidt, *Extrusion of Neoprene*, Du Pont Elastomers Bulletin NP-430.1, E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1987.
128. S. W. Schmidt, Calendering Compounds of Neoprene, Du Pont Elastomers Bulletin NP-440.1, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. 1987.
129. S. W. Schmidt, *Molding Neoprene*, Du Pont Elastomers Bulletin NP-450.1, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. 1987.
130. *Correlator for Baypren Polychloroprene*, Miles Inc., Technical Literature, 1992.
131. Ger. Pat. 1,186,215 (Jan. 28, 1965), K. L. Miller (to E. I. du Pont de Nemours & Co., Inc.): (U.S. Pat. 3655,827 (Apr. 11, 1972), J. B. Finlay (to E. I. du Pont de Nemours & Co., Inc.).
132. R. Musch and U. Eisle, Preprints of the ACS Rubber Division Meeting, Detroit, 1989, The American Chemical Society, Washington, D. C., 1989.
133. U.S. Pat. 3,042,652 (July 3, 1962) R. Pariser and R. D. Soufie (to E. I. du Pont de Nemours & Co., Inc.).
134. S. W. Schmidt, *The Neoprene T. Family*, Du Pont technical bulletin NP-240.1, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1977.
135. D. G. Coe, *Neoprene Latex Based Adhesives*, du Pont de Nemours Int. SA Geneva, 1991.
136. T. Fukuda, K. Kudo, and Y. D. Ma, *Prog. Polym. Sci.*, 1992, **17**, 875.
137. DuPont Dow Elastomers L.L.C., Neoprene Waterbase Polychloroprene, Liquid Dispersion Selection Guide, rev. 4, Oct. 2003.
138. DuPont Dow Elastomers L.L.C. Aquastik$^{\text{TM}}$ Technical Bulletin, Waterbase polychloroprene, revision Oct. 2003.
139. “Polychloroprene, Chemical Profile,” Chemical Market Reporter (April 29, 2002).
140. C. W. Stewart, Sr., R. L. Dawson, and P. R. Johnson, *Effect of Compounding Variables on the Rate of Heat and Smoke Release from Polychloroprene Foam*, Du Pont elastomer bulletin C-NL-550.871, 1974.
141. FDA Status of Du Pont Neoprene Solid Polymers and Latexes, bulletin NP-120.1, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., 1984.

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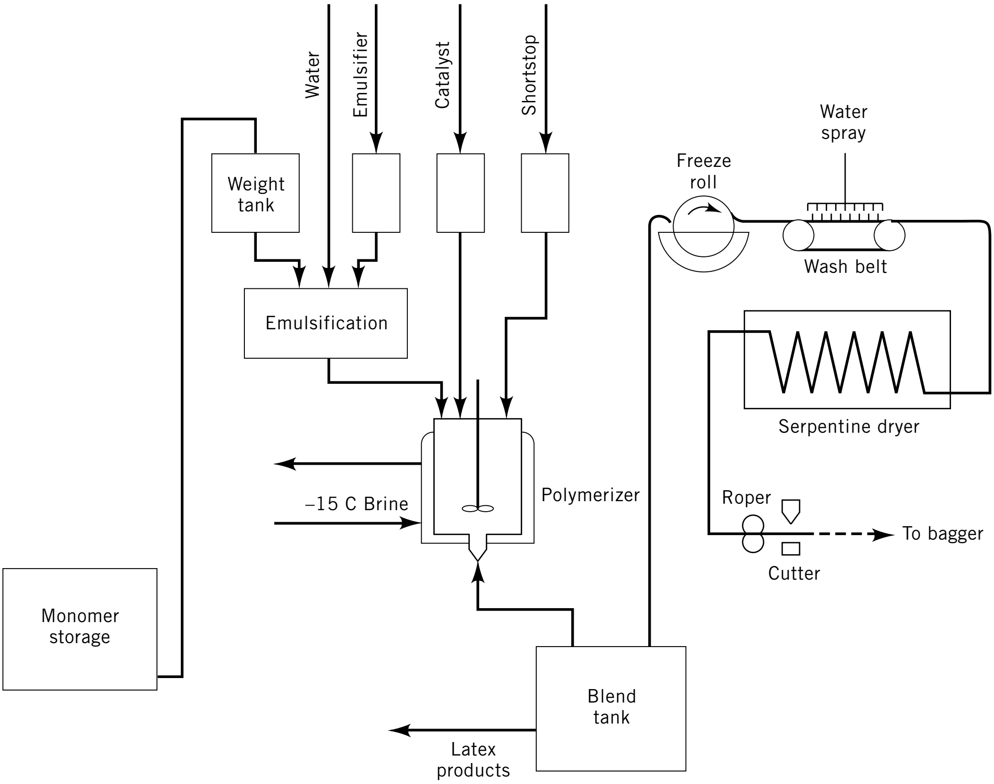

Fig. 1. Commercial manufacturing flowsheet (83).

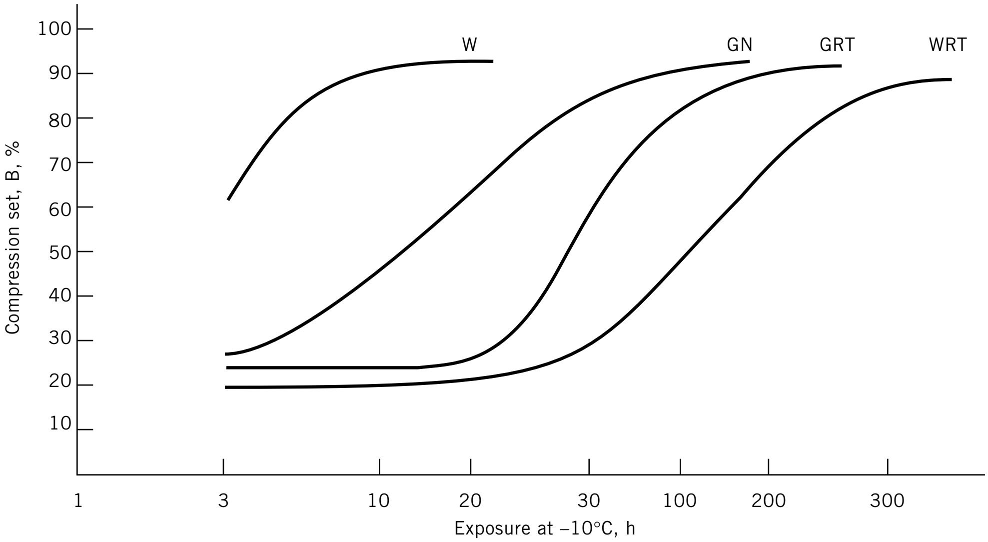

Fig. 2. Crystallization rate of polychloroprene vulcanizates under compressive stress (92).

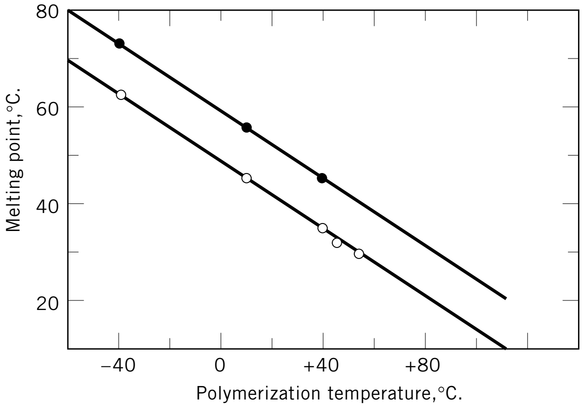

Fig. 3. Effect of polymerization temperature on the crystalline melting point of chloroprene rubbers produced by emulsion polymerization: •, highest observed value; ○, lowest observed value (93).

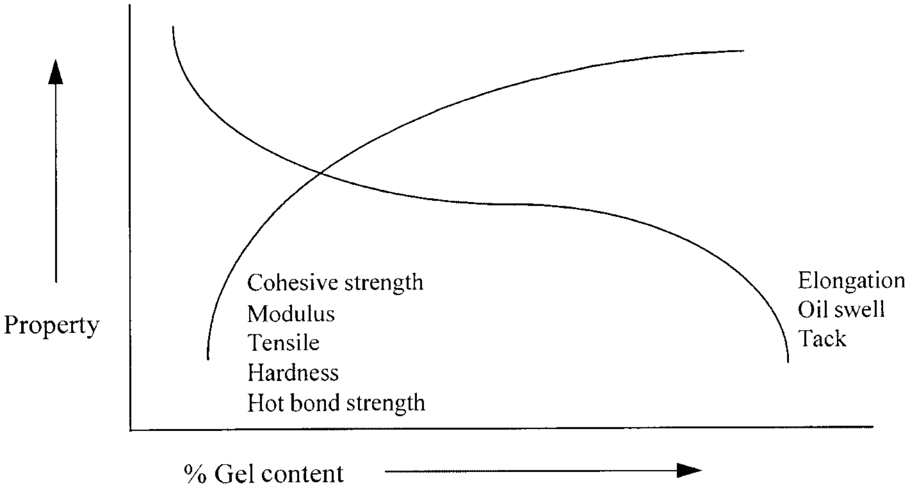

Fig. 4. Properties of polychloroprene latex as a function of gel content.

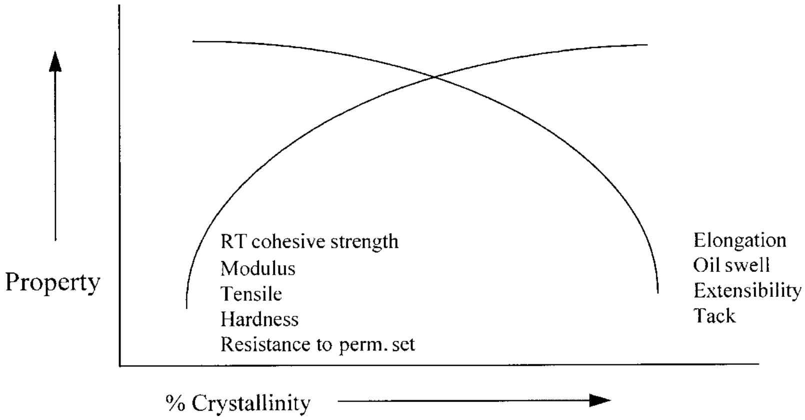

Fig. 5. Properties of polychloroprene latex as a function of crystallinity.

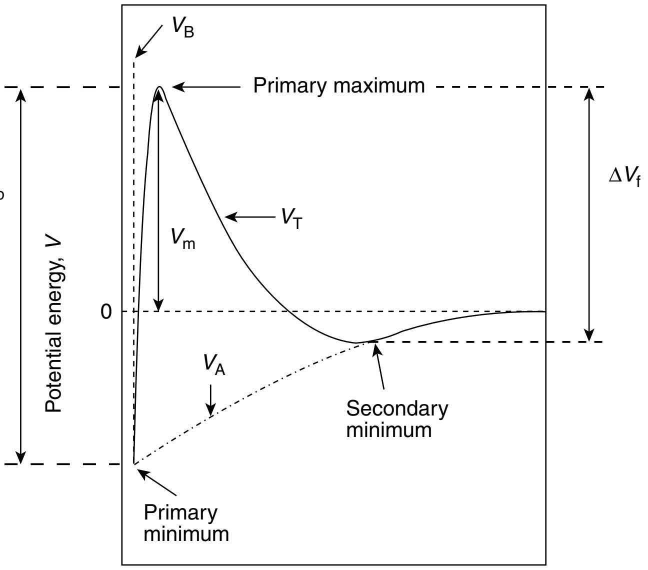

Fig. 6. Latex stability is potential energy.

Table 1. **Chloroprene (M1) Reactivity Ratios**

Comonomer M2	r_1	r_2
acrylonitrile	5.38	0.056
butadiene	3.41	0.06
2,3-dichloro-1,3-butadiene	0.31	1.98
1-(2-hydroxyethylthio)-1,3-butadiene	1.00	0.20
2-fluoro-1,3-butadiene	3.70	0.22
2-cyano-1,3-butadiene	0.14	2.8
diethyl fumarate	6.51	0.02
isoprene	2.82	0.06
methacrylic acid	2.7	0.15
methyl acrylate	10.40	0.06
methyl methacrylate	6.33	0.08
2,3,3-trifluoro-1-vinyl cyclobutane	2.71	0.64
styrene	5.98	0.025
sulfur	2–4	0.18

Table 2. **Microstructure of Polychloroprene by ^{13}C nmr**[a]

Polymerization temperature, °C	Z or trans 1,4 addition	Head-to tail 1,4 addition	E- or cis 1,4 addition	1,2 Addition tertiary allylic chloride	1,2 Addition isomerized primary allylic chloride	3,4 Addition
+90	85.4	10.3	7.8	2.3	4.1	0.6
+40	90.8	9.2	5.2	1.7	1.4	0.8
+20	92.7	8.0	3.3	1.5	0.9	0.9
0	95.9	5.5	1.8	1.2	0.5	1.0
−20	97.1	4.3	0.8	0.9	0.5	0.6
−40	97.4	4.2	0.7	0.8	0.5	0.6
−150	∼100	2.0	<0.2	<0.2	>0.2	<0.2

[a] Refs. 51,55.

Table 3. **Comparative Properties of Polychloroprene, EPDM, and Natural Rubber**

Property	EPDM	CR	NBR
density	0.86	1.23	1.0
hardness, Shore A	40–95	40–90	45–100
tensile strength, MPa	very low	21	very low 17
gum stock	>21	21	
black stock[a]			
service temperature °C	−50 to +150	−40 to +120	−20 to +120
heat resistance	high	moderately high	moderate
cold resistance	moderate	moderately high	low to moderate
T_{10} °C	−45	−45	−20
tan delta at 20 °C	–	0.09	0.1–0.18
set resistance	very high	moderately high	moderate to moderately high
tear resistance	moderate	high	moderate
aging resistance	moderate	high	moderate
ozone/corona resistance	very high	moderately high to high	moderate
aliphatic oil resistance	low	moderate to high	high
electrical resistance	high	moderate	moderate
bonding to variety of substrates	moderate	very high	very high
useful properties	excellent aging, medium strength	low damping, high weather/heat/oil resistance; good flex and tack	resists oils and chemicals, moderate heat resistance
limiting properties	self tack, poor composite building	moderate tensile, poor heat compared to EPDM	poor cold resistance

[a] Ref. 108.

Table 4. **Typical Dry Type Compound**[a]

polychloroprene	100
magnesia	4
stearic acid	0.5
antioxidants	2
antiozonants	2
fillers, processing aids, plasticizers as required	
accelerators	0.5
zinc oxide	5

[a] Ref. 110.

Table 5. **Plasticizers used for Polychloroprene Property Improvement**

Desired Property	Preferred Plasticizers
low cost	petroleum oils, naphthenic and aromatic
light colored or non-staining stocks (including black stock)	ester plasticizers, chlorinated paraffins or selected petroleum oils
low-temperature service	ester plasticizers or *cis*-polybutadiene
heat resistance	polymeric plasticizers, chlorinated paraffins, polyester plasticizers, and low volatility petroleum oils
low flammability	chlorinated paraffins and organic phosphate esters
fungus resistance	a polyether- [di (butoxy-ethoxy ethyl) formal
use with peroxide cure systems	ester, chlorinated paraffins or polymeric plasticizers

Table 6. **Attributes of the Various Classes of Plasticizers**

Plasticizers	Advantages	Disadvantages
organic esters, eg, dioctyl sebacate, butyl oleate[a]	best low-temperature brittle point	higher cost
	nonstaining, nondiscoloring	volatile leading to poor heat resistance
	useful for nonblack compounds	may craze plastics
	good compatibility	decreases stress-strain and tear
		increase crystallization rates[b]
petroleum oils	low cost	aromatic oil stain and interfere with peroxide cure
	general purpose	paraffinic oils have low compatibility
	aromatic oils have good compatibility	
	naphthenic oils have moderate compatibility	
chlorinated paraffins, eg, chlorowax, Chloroflo	better flame resistance than hydrocarbon rubber	Low plasticizer efficiency
	good low temperature properties	Increased smoke emissions
	can use in non-black stock	
	good heat resistance	
	moderate compatibility	
vegetable unsaturated oils (linseed and rapeseed)	good antiozonant properties	encourages fungus growth
	good heat resistance	
	retards sunlight induced discoloration	
polymeric ester plasticizers, eg, hexa-oxypropylene glycol monomethacrylate[c]	good heat resistance and low volatility	low plasticizer efficiency
resins, eg, coumarone-indene resins	improved building tack	reduced resilience
	improved heat resistance	reduced low temperature properties
	improved tear strength	
	high vulcanizate hardness	
	improved abrasion resistance	
	improved crystallization resistance	

[a] Refs. 85,125.

[b] Refs. 125.

[c] Refs. 124.

Table 7. **Standard Grades of Polychloroprene**

Product	Advantages	Limitations
General Purpose Grades		
chloroprene–sulfur copolymers	peptizable good building tack good tear strength good flex resistance low tan delta	poor heat resistance high compression set poor shelf stability
mercaptan modified homopolymers	easy molecular weight control good heat stability low compression set good shelf stability	not peptizable requires accelerator low flex resistance
sol/gel blends	improved rheology low nerve fast extrusion low die swell smooth extrudate surface collapse resistance better calendering	low tensile
Crystallization Resistant Grades		
copolymers of 2,3-dichloro-1,3-butadiene, styrene	low crystallization rates	slightly higher T_g
high temperature and high pressure polymerization	low crystallization rates	poorer heat resistance
Adhesive Grades		
low temperature polymerization	rapid crystallization rapid solubility in organics adheres to wide variety of substrates	thermal stability cannot be used if gelled
Specialty Grades		
xanthogen disulfide modified homopolymers and copolymers	high stress-strain faster cure rate low tan delta low compression set	poorer heat resistance than mercaptan modified types
Latex		
emulsion polymerization	high solids good film former gelled polymer for adhesives environmentally desirable for solvent-free adhesives	freezes poor thermal stability sensitive colloid system

Table 8. **Comparison of Properties of Anionic and Nonionic Polychloroprene Latexes**[a]

Property	Anionic	Nonionic
surfactant type	sodium or potassium resinates	poly(vinyl alcohol)
colloidal stabilization mechanism	electrostatic	steric
stability		
mechanical	good	exceptional
electrolytic	good	excellent
to ionic contaminants	poor-fair	excellent
storage	good	gel increases
pH	12+	7–8
% solids	38–60	47
surface tension (mN/m)	39	58
brookfield viscosity mPa.s	5–500	500
average weight average particle size (nm)	100	300

[a] Ref. 135.