

# Chapter 3

## Polyvinyl Chloride (PVC), Chlorinated Polyethylene (CPE), Chlorinated Polyvinyl Chloride (CPVC), Chlorosulfonated Polyethylene (CSPE), Polychloroprene Rubber (CR)—Chemistry, Applications and Ecological Impacts—I



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**Abstract** As every coin has two sides, similarly polymers are playing an important role in our daily life as well as are creating pollution in the environment. Polymers have been part and parcel of emerging fields of science and technology. The word polymer is derived from the Greek words “poly” and “meres” which means ‘many’ and ‘parts’. Polymers are macromolecules that are produced by the repetition of small molecules called monomers. Cellulose, protein, starch, and natural rubber are the examples of natural polymers. Polyvinyl chloride is a product of free radical polymerization of vinyl chloride. Substitution of hydrogen atoms in high-density polyethylene by chlorine atoms will produce chlorinated polyethylene. Chlorinated polyvinyl chloride is a thermoplastic polymer that is produced by chlorination of polyvinyl chloride by free radical chlorination reaction. Commercially available polymer Teflon is chemically chlorosulfonated polyethylene. Polychloroprene rubber is synthesized by emulsion polymerization of chloroprene. Different polymers have different aspects as polyvinyl chloride is applied for the making of rigid pipes, flooring, etc. Chlorinated polyvinyl chloride is compounded with other ingredients to get desired properties according to various applications. The properties of chlorinated polyethylene depend on the chlorination of polyethylene, which makes it suitable in the production of wires, cables, coal mine cables, etc. Chlorosulfonated polyethylene has been used widely for protective coatings, electrical cable jacketing, roof shielding, etc. Polychloroprene is being used in car fan belts, gas kits,

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mouse pads, corrosion resistance coating, etc. Some of these synthetic polymers have adverse effects on the environment, flora, and fauna.

**Keywords** Chlorination · Monomers · Macromolecules · Polymerization · Synthetic

### 3.1 Introduction

Polymers have become an integral part of our lives. The word polymer evolved from a Greek word that means many parts. Proteins, carbohydrate, starch, cellulose, and rubbers are those natural polymers which have an existence from the origin of life. These polymers are categorized as natural and synthetic based on their origin. Polyethylene, polyvinyl chloride, polystyrene, bakelite, and synthetic rubbers are very well-known polymers in the world of plastics. Polymers are those macromolecules that are formed by the repetition of macromolecules known as monomers. The process of repetition of monomers is known as polymerization. These macromolecules are exhibiting exclusive properties of high molecular weights, viscoelasticity, and glass transition temperature. The credit to discover the term polymers goes to a Swedish chemist, Jöns Jacob Berzelius in 1833 (Mustafa et al. 2013).

Many years have been dedicated by scientists to create the engrossing world of polymers. In 1820, rubber was considered a polymer but its properties like fluidity and blending were discovered by Thomas Hancock for molding purposes. After some years in 1839, Charles Goodyear worked on the advancement of properties of the rubber by heating with sulphur. This innovation was patented by Goodyear in 1844.

In 1846, an invention of Christian Friedrich Schönbein came into the picture in the form of cellulose nitrate or Gun Cotton which was an explosive polymer with good molding properties at high temperatures. Later on, methyl rubber was manufactured from 2,3-dimethyl butadiene as the first synthetic rubber in Germany. A new concept was proposed by Hermann Staudinger in 1920 that polymers are macromolecules with covalent bonds. The Nobel Prize for chemistry was awarded to Paul Flory for his incredible contribution in the field of polymeric science (Young and Lovell 2011).

### 3.2 Types of Polymers

There are different types of polymers which are playing different roles according to need. Polysilanes, polysilazanes, polysulfides, polyphosphazenes, polyborazylenes, polythiazyls and polysiloxanes are inorganic polymers in which the polymeric backbone is made up of inorganic atoms. Organic polymers are those polymers in which the backbone is composed of carbon and other atoms. These organic polymers are further classified into synthetic and natural polymers:

**Natural Polymers**—These are the organic polymers that are found in nature. The basic composition of the human body is based on natural polymers like protein and nucleic acids. Organic polymer cellulose is the fundamental structure of plants similarly the main component of food is starch.

**Synthetic Polymers**—Synthetic polymers are those polymers that can be synthesized. Thermoplastics and thermosetting are further classifications of synthetic polymers. Thermoplastics can change their shape at a particular temperature. Polyvinyl chloride, nylon, polyethylene, polypropylene, and polystyrene are some examples of thermoplastics. Thermosetting are those polymers that cannot be reheated, reshaped, and reused. Bakelite is a common example of thermosetting (Gad 2014).

### 3.3 Polyvinyl Chloride (PVC)

Polyvinyl chloride (PVC) is the most commonly used synthetic polymer with CAS number 9002-86-2. It is produced by the addition of the vinyl chloride monomer. On large scale, polyvinyl chloride is manufactured from vinyl chloride monomer in presence of free-radical initiators by using the suspension, bulk, solution, and emulsion polymerization. In comparison to most plastics, PVC is much denser at 20 °C; the density is 1.37–1.43 g/cm<sup>3</sup>; 1.53 g/cm<sup>3</sup> (crystalline); 1.373 g/cm<sup>3</sup> (amorphous), melting point is 103–230 °C and glass transition temperature is 87 °C. Rigid PVC is very hard with extremely good tensile strength.

In 1835 and 1872, Henri Victor Regnault and Eugen Baumann were acknowledged for the discovery of polyvinyl chloride. Later on, in 1913 the first patent for the polymerization of vinyl chloride in the presence of sunlight to form PVC was granted to the German chemist Friedrich Heinrich August Klatte. Waldo Semon, in 1926 gave new dimensions to PVC by discovering the process of plasticization (Wypych 2016).

Polyvinyl chloride is a thermoplastic material and has been part of our lives. There are many methods of its synthesis given in the literature. Pure PVC is a mechanically tough, rigid, electrically insulating material that shows good water, weather, and chemical resistance, but it is unstable towards light and heat. In the presence of UV light and heat, hydrogen chloride (HCl) formation occurs due to loss of chlorine, which can be prevented by using stabilizers. Generally, these stabilizers are composed of salts of metals like calcium, barium, cadmium, or lead [COM (2000) 469-C5-0633/2000-2000/2297(COS)].

PVC is synthesized by the chain polymerization of the monomer, vinyl chloride. Vinyl chloride is prepared from the reaction of chlorine (57 wt%, manufactured by the chlor-alkali electrolysis) and ethylene (43 wt%) (Pascault et al. 2012). PVC shows good thermal, mechanical stability and poor shielding ability towards ultraviolet (UV) light because of this reason the applications of polyvinyl chloride (PVC) are limited. To improve the characteristics of PVC, a hybrid nanostructure containing layered double hydroxides (LDHs) and  $\alpha$ -Manganese oxide ( $\alpha$ -MnO<sub>2</sub>) nanorods were used. In the first step with the help of bio-safe molecules, LDH and  $\alpha$ -MnO<sub>2</sub> nanorods were modified to make them adaptable to the PVC matrix. In the second step, different

weight percentages of the resulting nanohybrid like 5, 10, including 15 wt% were introduced to the polyvinyl chloride. In the third step, different analyses of resulting nanocomposite films were identified. It was observed that UV-visible absorption spectra of nanocomposites show an enhanced absorption peak as compared to the pure polyvinyl chloride (Mallakpour and Naghdi 2020).

### 3.3.1 Applications

PVC is a widely used valuable polymer. Polyvinyl chloride (PVC) products are physically and chemically recyclable. PVC is a thermoplastic used to make various household products such as kid's houses, shoe stands, laptop stands, kid's scooters, bookshelves, etc. The improved properties like high impact resistance, good temperature capability, lightweight, etc. make PVC capable of replacing building materials such as clay, metal, concrete, and wood used traditionally in many applications. Nowadays, PVC acts as a 'wonder material' which can be used in different ways to make useful products, and one of the most popular products among them is PVC furniture (Khan and Malvi 2016).

PVC can be treated easily, and has excellent basic properties. It is flexible and inexpensive hence suitable for the piping industry. Thermally PVC is a sensitive thermoplastic therefore a large number of compounds like heat stabilizers, processing aids, pigments, lubricants, impact modifiers, and fillers must be added to stabilize it. U-PVC (Unplasticized polyvinyl chloride) has great resistance towards chemicals so it is suitable for merging with the polished surfaces of the internal pipe wall to minimize scaling for a better service life of pipe with excellent flow characteristics (Walsh 2011). PVC is biologically and chemically resistant which makes it desirable for most household corrosion-resistant sewerage pipe applications (Ameer et al. 2013).

Nearly 25% of plastic materials used as medical products are made of polyvinyl chloride. Plasticized PVC has transparency retention and good clarity which allows monitoring of fluid flows in tubes and its resistance towards kinking. It prevents the risk of interruption in fluid flow through tubes (McKeen 2014).

A systematic study has been carried out in Las Vegas to use electroactive and transparent plasticized polyvinyl chloride (PVC) gel as a soft actuator for tiny mechanical devices, synthetic muscle applications, Opto-electro-mechanical devices, and optics (Hwanget al. 2019). Phthalates are plasticizers of PVC which are used widely in food packaging applications. This plasticized PVC can also be used to make certain food processing equipment like tubing and conveyor belts. However, due to the hazardous effects of phthalates, other compounds can be used to replace these phthalates (Carlos et al. 2018).

### 3.3.2 Ecological Impacts

Polyvinyl chloride (PVC) is mainly used as a flooring material, building material, food packaging material, piping material, and various household materials. At different intervals in the vinyl lifecycle, many harmful by-products like organochlorine get formed and escape into the environment which can harm human health and the environment.

Numerous health hazards like birth defects, dysfunction of the endocrine system, cancer, neurotoxicity, and suppression of the immune system have been caused due to feeding stocks and by-products produced at different intervals in the vinyl lifecycle. Many bioaccumulative substances are also found in the different stages of the PVC lifecycle, which are oil-soluble in nature, and can intensify negative effects as they move to higher levels in the food chain. These bioaccumulative substances easily cross the placental barrier and are able to deposit in the mother's milk of mammals (Thornton 2007).

PVC is a major cause of dioxin formation, which is a true global pollutant, now the presence of dioxin has been investigated in animals, humans, in the tissues of whales and polar bears. Dioxins hold the potential to cross the placental barrier easily and to be deposited in a mother's milk. As a result, infants consume high doses of dioxin in comparison to adults. During formulation, phthalates are mixed with polyvinyl chloride which causes various health effects like reduction in sperm count, testicular damage, infertility, and damaged reproductive system (Thornton 2007).

The locally manufactured pipes were investigated to observe the movement of its vinyl chloride monomer (VCM) from unplasticized polyvinyl chloride. For this purpose, a study was carried out at different time intervals using variables such as total dissolved solids, pH, and temperature in water. The strength of VCM in the running water of pipes was evaluated using the head-space technique or gas chromatography. After exposure, at 45 °C for 30 days the VCM concentration was detected at more than 2.5 ppb in water. It was observed that the migration of VCM remains unaffected to water temperature unless it was raised to 45 °C (higher value) whereas total dissolved solids (TDS) and pH of water were identified to affect the movement of PVC monomer (vinyl chloride) from unplasticized polyvinyl chloride pipes (Muhammad et al. 2000).

An experiment was carried out in Romania to observe the impacts of PVC on environmental factors by the production process of PVC. The study showed that the process hurts the environment with photochemical ozone creation potential (POCP), high contribution to AP (acidification potential), GWP (global warming potential), and HTP (human toxicity potential). The main contributors to HTP are dioxins emitted during the production of vinyl chloride whereas emissions of the volatile organic compound during the processing of crude oil lead to photochemical ozone creation. During various stages in the process, the consumption of energy contributes to climate change while the emitted substances cause acidification (Comaniță et al. 2020).

The health and environmental impacts of vinyl chloride monomer (VCM) in the PVC industry is classified as Group A by the EPA (US Environmental Protection Agency) as a carcinogen to humans (US EPA 2000).

### 3.4 Chlorinated Polyethylene (CPE)

This thermoplastic is produced by chlorination of polyethylene in solution or powdered form at elevated temperature. Chlorinated Polyethylene (CPE) was discovered by Fawcett, EW; Gibson, RO; Perrin MW in the year 1939 (Wypych 2016).

There are various ways to chlorinate polyethylene, chlorination can be performed in a solution where solvent should be non-reactive to chlorine. Polyethylene can also be produced by aqueous suspension, solvent suspension, melting, solid-phase, and block chlorination. Various forms of polyethylene like powdered, granulated, fibrous, and thin-film are the preferred choices. Carbon tetrachloride, chlorobenzene, and ethane tetrachloride are commonly used solvents for chlorination. Chlorination through a diluted solution of polyethylene is the best way to get chlorinated polyethylene of desired properties with uniformly distributed chlorine. The JCI company of Great Britain invented the process of chlorination in the gaseous form of chlorine by utilizing low-density polyethylene suspension in presence of carbon tetrachloride or acetic acid solvents and metal chloride (Donskoi et al. 2003).

Researchers put much effort into this polymer to make it more usable. To obtain various CPI of different properties like hard, brittle to elastic at different conditions, a mixed solution suspension technique was used to chlorinate Low-density polyethylene (LDPE) at three different temperatures. Through various characterizations (static mechanical, chemical and thermal), two different crystal structures were predicted which disappeared during chlorination (Akovali and Vatansever 1986).

Graft copolymerization is a way to form a polymer of distinctive properties. Hence to intensify, thermal and mechanical properties of CPE, chlorinated polyethylene-chlorinating/grafting-poly (acrylic acid) and its sodium salt ionomer were prepared by in-situ chlorination graft co-polymerization. This Grafted copolymer was fabricated with a CPE backbone and polyacrylic acid branches. This Grafted copolymer and its carboxylated ionomer were subjected to Fourier Transform-Infrared (FTIR), to get gel permeation chromatography and degree of grafting report. The effect of various factors like reaction temperature, chlorine content, monomer concentration of the product was studied to describe the reaction (Wang et al. 2012).

In the same way, a dedicated team of Wang et al. (2014) worked on gas solid-phase chlorination to get grafted polymer of maleic anhydride for low-density polyethylene. This synthesis was patented (in situ chlorinating graft copolymerization) in which two problems were sorted out with a novel approach. The first problem was chlorination and grafting feasibility at the same time on low-density polyethylene molecular chains and the second was to regulate control of highly chlorinated polyethylene synthesis. Fourier transform and 1-hydrogen nuclear magnetic resonance (1H-NMR)

techniques were applied to check the feasibility of chlorination. Gel permeation chromatography, stereoscopic microscopy, and chlorine content versus time curve were used to analyze the sample's molecular weight, distribution thermal properties, and agents that affect the chlorination process. The degree of grafting was observed at 2%. Adhesion and impact strength tests were also applied to check the feasibility of the polymer (Wang et al. 2014).

In the presence of ultraviolet light, high-density polyethylene (HDPE) was chlorinated (radical chlorination) by an aqueous slurry process under moderate pressure. In the experiment, two temperature conditions were applied in two steps, below and above the crystalline melting point. Three products were obtained with a chlorine concentration of 6.5, 12 and 34% by weight of HDPE. The FTIR spectrum of all three samples was taken and compared with polyethylene and polyvinyl chloride to confirm reaction progress. Flask combustion method (DIN EN ISO 1158)—an elemental analyzing technique was applied to check chlorine content (Razmirad and Moradi 2012).

In this study, the composition and microstructure of chlorinated polyethylene were determined by the pyrolysis gas chromatographic method. Pyrolysis of CPE polymer generates aromatic compounds through dehydrochlorination of the trimer at high temperature. The different levels of formed ethylene and vinyl chloride trimers decided composition and microstructure. <sup>13</sup>C NMR analysis is helpful for the structure elucidation of CPE polymer having 25–48% chlorine (Wang and Smith 1997).

Blending is a technique to get a better product in polymer science. To this, an effort has been made to synthesize blends of CPE, PVC, and poly alpha-methylstyrene-acrylonitrile in a ratio of (70/30). The outcome of the investigation was that the addition of CPE improved the toughness and heat stability without impacting the heat resistance (Zhang et al. 2010). For the advancement of physico mechanical characteristics of polyvinyl chloride, a blend of PVC and CPE was prepared. The result is that the addition of CPE improved the impact strength, electrical properties, and fire resistance but the brittle point was not improved. These changes were dependent upon the ratio of PVC and CPE in blends and chlorine content of CPV. In this study, factors like thermo rheological, residual crystallinity, compatibility, applicability, and principle of temperature–time suspension were studied. Some modifiers were added to upgrade elasticity, impact strength and to reduce elastic modulus and strength of quasi-static tension. The impact strength of PVC and CPE could also be enhanced by adding polystyrene. Morphological study of blended samples confirmed that nano-sized polystyrene will create a spatial network (Maksimov et al. 2003).

For manufacturing of plastic runway or rubber hose, composite of chlorinated polyethylene/industrial waste red mud/carbon black were synthesized where ratios of red mud/carbon black were 40/20, 20/40, 10/50, 5/55 and 0/60. All synthesized samples were subjected to testing the mechanical and thermal properties. The addition of red mud to chlorinated polyethylene/carbon black raised the tensile strength of a composite by 10–14 MPa and thermal degradation was increased by 10 °C. After three days, hardness and tensile strength of different composite samples were further increased by 10 shore A and 2 MPa. The study concluded that composite sample

was more stable thermally when red mud (20 phr) and carbon black ratio was 20/40. The Payne effect was also reported by the rubber process analyzer. It was found that composite prepared by 20 phr red mud has good properties (Qiu et al. 2020).

### 3.4.1 Applications

CPE, a good general-purpose oil, has the resistance against heat and ozone. The CPE is synthesized by chlorination of HDPE by the free radical aqueous process. The product has chlorine content of 36–48%. A research was conducted on the blending of chlorinated polyethylene with polyvinyl chloride, polypropylene, and styrene-acrylonitrile to upgrade mechanical properties like impact strength, breaking elongation, and tensile strength (Iranmanesh and Shafiei 2012).

A thin film of 8–10  $\mu\text{m}$  is fabricated by randomly prepared CPE (71% chlorine by weight of PE). Here, high chlorine content is accountable to increase glass transition temperature (110  $^{\circ}\text{C}$ ) and Young's modulus (2.6 GPa), these increased parameters can also elevate breakdown strength. For restricted loss at elevated temperature and well-maintained medium permittivity (3–4), random dispersion of chlorine atoms is playing a pivotal role. The changed parameters resulted in high energy density (12 J/CM<sup>3</sup>) and high discharging efficiency (83%) under an electric field of 700 MV/m. So these parameters can make CPE a polymeric dielectric material for high pulse metalized film capacitors (Zhao et al. 2018).

It was reported for the first time that UV radiation can accelerate the rate of chlorination. A vibrated-bed reactor was used to study the kinetics of thermal and UV enhanced gas–solid HDPE chlorination at that temperature which was below the melting point. The kinetics of chlorination was recorded with the help of a UV-Visible spectrophotometer. Even chlorinated products had no chlorinated crystal structures with small content of chlorine. In this mechanism, to minimize residual crystallinity and to increase the homogeneity of chlorination, multi-stage chlorination was suggested. The presence of  $-\text{CH}=\text{CH}-$  bonds in CPE assured that chlorination occurred at 150  $^{\circ}\text{C}$ . One more observation was remarked by differential scanning calorimetry that when the temperature was beyond the melting point, melting enthalpy was decreased effectively (Zhang et al. 2018).

The most common application of CPE is as an impact modifier for PVC which can increase the toughness of PVC and another chemical Dioctyl phthalate (DOP) is known to increase the plasticity of PVC. The samples of varied CPE and DOP were subjected to tensile strength and breaking elongation testing at changed hot-pressing temperatures. The result of the study was in reduction of tensile strength and up-gradation of breaking elongation. Mechanical properties and blending effects of CPE and PVC samples were raised by raising the hot-pressing temperature. DOP has the potential to precipitate at hot pressing temperatures (Xie et al. 2011).



### 3.4.2 Ecological Impacts

Many studies have been conducted to inspect the adverse effect of polymers on the marine ecosystem. The water pollution generated by plastics is a major concern for the environmentalists. A study has been conducted on the presence of microplastics (MPs) in the Gulf of Guinea (Ogun and Osun Rivers) in Nigeria. The 29 samples of three insect species have been analyzed by micro-Fourier-transform infrared ( $\mu$ FTIR) spectrophotometer and digital microscope. Results showed that CPE was found in *Chironomus* sp. of Ogun River (Akindele et al. 2020).

Hydrochloric acid and carbon monoxides are combustion and degradation products of CPE which are known to produce carcinogenic activities. Small particles of CPE are also injurious for eyes and skin so precautionary measures are required to work with CPE. To enhance the properties of CPE, additives are added which can release volatile organic compounds at high temperatures (Akovali 2012a, b).

## 3.5 Chlorinated Polyvinyl Chloride (CPVC)

The synthesis of chlorinated polyvinyl chloride (CPVC) is an example of hydrogen atom substitution from a polyvinyl chloride (PVC) molecule by a chlorine atom. This substitution is followed by a free radical mechanism. Heat and ultraviolet radiation are required to initiate the reaction. CPVC was invented by Schoenburg of IG Farben Industries in 1934, who also demonstrated that chlorinated PVC contained 64–68% of chlorine. The trade name of this thermoplastic is Geon (Wypych 2016). This thermoplastic has also been an interesting topic to researchers for its excellent properties. Many methods of its synthesis have been suggested from time to time.

Lu et al. (2011) worked on the plasma-assisted synthesis of CPVC (containing 67% of chlorine) by the gas–solid contracting process. The produced CPVC was found to be comparable to the commercial CPVC in mechanical properties, thermal stability, and microstructure. In this mechanism, the cold plasma generated free radical chlorine played an active role in surface activation of PVC. This reaction was decoupled into two steps. In step one, on the particle's surface chlorination occurred which was enhanced by plasma and in the second step, migration of chlorine occurred from the surface to the core in the dielectric barrier discharge plasma fixed bed reactor. After the complete cycle of 3 h, CPVC was produced with 67% of chlorine content. The characterization of the sample was carried out with the help of scanning electron microscopy, thermogravimetric analysis, and Raman spectra (Lu et al. 2011). In another new approach, PVC was subjected to preliminary foaming treatment for the chlorination process. The reaction was accomplished in the presence of supercritical carbon dioxide and acetone. The experiment resulted successfully in the form of increased content of chlorine as 0.66 g/g for PVC which was treated before chlorination. On the other hand, non-pretreated PVC had only 0.60 g/g chlorine content. The result was compiled based on gel permeation chromatogram, differential

scanning calorimetric analysis and  $^{13}\text{C}$  carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectrum. CPVC which was pretreated had given the proof of fine thermal properties, narrow molecular weight distribution, and uniform distribution of chlorine (Qian et al. 2017).

Yang et al. (2015) used plasma circulating fluidized bed reactors for plasma-assisted synthesis of CPVC. CPVC has been advised to be superior thermoplastic than PVC for heat stability, mechanical and flame retardation properties because of the enhanced polarization effect of chloro group on PVC. These two stepped decoupled chlorination processes performed as a slow diffusion mechanism. In both steps, polymer surface and reactive gas activation occur by plasma, and migration of absorbed chlorine proceeds to the core of the polymer. This was a novel approach to synthesize CPVC in plasma circulating fluidized bed reactor rather than the traditional way to synthesize by an aqueous suspension. The final product was characterized by scanning electron microscopy and Raman spectrum which indicated the presence of fine microstructure and uniform chlorine distribution.

A methodological work has been done to identify the ability of CPVC in making heterojunction with Tin (Sn) and Titanium (Ti) compounds. This CPVC/SnS<sub>2</sub>/TiO<sub>2</sub> (Chlorinated Polyvinyl Chloride/Stannous Sulphide/Titanium dioxide) heterojunction has been recognized as an innovative, highly effective, visible-light-driven ternary photocatalyst. The photocatalytic test signified that CPVC/ SnS<sub>2</sub>/TiO<sub>2</sub> heterojunction is an effectual photocatalyst for photocatalytic reduction of aqueous chromium salt and photocatalytic degradation of methylene blue in electromagnetic radiation of visible region (Liu and Zhang 2021).

Merah et al. (2013) tested the tolerance power of CPVC pipes against the worst environmental conditions. Natural and accelerated artificial weathering is a major cause to affect the mechanical, physical, and chemical properties of CPVC pipes. Various observations have been noticed by applying different testing-sample of CPVC pipes kept in natural outdoor environments for duration of two weeks to eighteen months under UV exposure of 100–3000 h. THE same CPVC sample was examined for the tensile strength test. The outcome of the study was, the strength and stiffness of CPVC samples have been affected to a small extent by natural and accelerated weathering. Artificial UV exposure of 100 h and natural weathering (duration 15 days) caused a reduction in fracture strain. The physical examination of the CPVC sample approved that both types of weathering generated gradual discoloration in samples. Attenuated total reflection infrared (ATR-FTIR) and Ultraviolet-Visible (UV-Visible) spectroscopy confirmed that dehydrochlorination was responsible for the degradation of CPVC (Merah et al. 2013).

### ***3.5.1 Applications***

CPVC is a polymer of substantial importance in industries because of its excellent chemical resistance, anti-corrosion, good mechanical, physical, low flame, and

low smoke spreading properties. CPVC is a popular thermoplastic in making chemical processing pipes, pulp processing pipes, paper processing pipes, water treatment pipes, sewage treatment pipes, food processing pipes, residential hot-cold water plumbing pipes, industrial-residential sprinkler pipes, fittings, and valves. The uniqueness of CPVC is to provide a higher temperature service range. Many CPVC products can be operated at 200 °F. For hot corrosive liquids, CPVC is an ideal material at 210 °F. CPVC acts as glue for solvent cement. At 73 °F, CPVC and PVC reveal the same physical properties (Walsh 2011). CPVC resin is considered a multipurpose material for various industrial applications because of its anti-corrosion, high mechanical, smoke suppression, and heat retardant properties (Xin et al. 2017).

CPVC pipes are designed to resist the worst conditions of temperature and pressure. Research has been performed in Saudi Arabia to observe the adverse effects of environmental conditions on CPVC pipes. The samples were prepared from locally available CPVC pipes, which were subjected to standard tensile and single edge notched tension (SEN) fracture toughness tests for duration of 1–9 months. The result revealed that adverse environmental conditions affected tensile strength and elasticity minutely, but the surface of the sample was affected severely. The study concluded the environmental tolerance of CPVC at high temperature and pressure conditions. Therefore, the use of CPVC is gaining popularity in the plumbing industry (Merah 2007). CPVC has been a well-recognized polymer in US markets since 1982. The proposal was submitted to the California Building Standards Code in February 2007 to get approval for the installation of chlorinated polyvinyl chloride pipes in the domestic water supplying system. The limited use of CPVC pipes has been approved based on an environmental impact report issued by the department of housing and community development (Martins et al. 2009).

On controversial notes, the use of steel pipes has faded away in fire protection systems because of these CPVC pipes which are low priced and can be installed very easily. On the other side of the coin, the use of CPVC pipes is unsuccessful in comparison to steel pipes. The impact, environmental stress cracking, high pressure, and manufacturing defects are some challenges in the path of CPVC pipes applications. As a consequence, more research is required to overcome these issues for application purposes (Hayes et al. 2010).

### ***3.5.2 Ecological Impacts***

CPVC pipes are a desired product of the market for drinking water distribution systems but the monomer vinyl chloride used in the synthesis of CPVC is carcinogenic in nature. This vinyl chloride can leach from CPVC pipes into drinking water. In a study by Walter et al. (2011), different levels of vinyl chloride accumulation were analyzed from samples of different sources. Pieces of evidence showed that vinyl chloride can also be accumulated as a disinfection by-product. The presence of organotins in water is another threatening issue which is caused by plastic pipes.

Keeping this threat in view, a study was carried out to check the possibility of organotin leaching of heat stabilizers and organic compounds into the water. These organic compounds are the main component of organic solvents, and these organic solvents are used to seal CPVC pipes. Various analytical techniques were applied to check the availability of these toxins in the water. In experimental work, samples of PVC and CPVC pipes were subjected to hydride generation atomic absorption spectroscopy, gas, and mass chromatography. There was an observation that leaching of organotin and organic compounds occurred in a biphasic manner. The outcome of the study was that the concentration of dimethyl tin dichloride, butyl tin dichloride, methyl ethyl ketone, tetrahydrofuran, and cyclohexanone obtained 10 ppm to 10 ppb in exposed water samples which is hazardous for health and creating new problem statements for researchers (Boettner et al. 2002).

### 3.6 Chlorosulfonated Polyethylene (CSPE)

Chlorosulfonated polyethylene (CSPE) was discovered in 1940 by McQueen DM at DuPont (DuPont 2007). This chlorosulfonated polyethylene contains 24–43% chlorine and 1.0–1.4% sulfur. Acsium and Hypalon are the trade names for CSPE and the CAS number is 9002-88-4. At 20 °C, the density of CSPE is 1.0–1.27 g/cm<sup>3</sup>, melting point is 87–140 °C and glass transition temperature ranges from 7 to –27 °C. It is white to slightly yellow in color with an ether-like smell and flame resistance. In comparison to neoprene and butyl rubber, it possesses better weather and ozone resistance. CSPE elastomers exhibit much better abrasion resistance and mechanical properties than CPE (Wypych 2016). This is a valuable and marketable polymer. Many investigations have been conducted on this polymer.

**Preparation of chlorosulfonated polyethylene using a gas, solid, and liquid three-phase reaction:** In this invention, the preparation of CSPE comprises the addition of chlorinated polyethylene powder into a multilayer stirred fixed bed reactor along with an anti-adhesive agent, followed by the exposure to atomized sulfonyl chloride under ultraviolet irradiation. During the process according to the weight of the chlorinated polyethylene, a total of 4 to 15% sulfonyl chloride was added by maintaining the temperature below 80 °C. A finished product of CSPE was obtained after rinsing with water, centrifugal dehydration followed by drying in hot air (CN102153683A).

In this methodology, the synthesis of chlorosulfonated polyethylene was performed by the suspension method. Chlorinated polyethylene with chlorosulfonation reagent was suspended in a solvent. The resulting suspension was induced either by ultraviolet light or an initiator at a certain temperature to form chlorosulfonated polyethylene as a product which on filtration followed by washing and drying results in white powder (CN104725534A).

CSPE was synthesized in the presence of an initiator by the reaction of a combination of chlorine and sulfur dioxide, chlorine and sulfonyl chloride, or a weak base and sulfonyl chloride with polymers. The resulting polymer may contain 1–5% sulfur

and 20–60% chlorine as sulfonyl chloride groups. The parent polymer crystallinity has been destroyed by the chlorine atoms which resulted in better chemical properties like resistance towards heat, ozone, oxidizing chemicals, and oil. Due to the presence of the sulfonyl chloride group, chlorosulfonated polyethylene can combine with bivalent metal sulfides, radical traps, or oxides to form stable compounds with cross-linkage (Ennis 2000).

Chlorosulfonated polyethylene was synthesized using a mixture of dioxide sulfur and chlorine along with chlorinated polyethylene in a tank reactor. The results of the investigation showed that elevated reaction temperature from 30 to 50 °C directly leads to accelerate the rate of chlorosulfonation with higher sulfur content (Zhao et al. 2001).

### 3.6.1 Applications

Chlorosulfonated polyethylene has many advantages over other polymers like polyolefins and polyvinyl chloride. It is a synthetic rubber produced from polyethylene and is popular for its excellent resistance towards ultraviolet light, chemicals, and temperature (30–130 °C) (Akovali 2012a, b). The resistance to a wide range of temperature makes it suitable for various industrial applications.

Chlorosulfonated polyethylene is widely used in construction and industrial applications where high performance is needed. In the automobile sector for the year 2008, its consumption was nearly one-fourth of total world consumption. In the construction sector, it is used as liners and roofing membranes for reservoirs and ponds (Akovali 2012a, b).

A systematic work has been carried out on fast-changing technology for electric vehicles using polymeric insulated cable made of chlorosulfonated polyethylene sheath and ethylene-propylene-diene insulation having an excellent thermal performance with high current carrying capacity. By this application, the thermal conductivity was modified for both the materials using hybrid boron nitride. The outcome of the study appears as a significant improvement in the current-carrying capacity with excellent mechanical and electrical–mechanical properties (Du et al. 2019).

Bulgakov et al. carried out a study to observe the improvement in the adhesive strength of rubbers with the use of modified chlorosulfonated polyethylene. This modification was made with the use of amino-containing compounds. It was analyzed that the adhesive strength of the compositions to resins increases by two to five times with these modifications. Chlorosulfonated polyethylene has important properties like resistance towards the fire, abrasion, atmospheric action, and chemicals which made it a better choice for the composition of coatings, enamels, sealants, prime coatings, and adhesives (Bulgakov et al. 2012).

To enhance the strength of adhesive joints between vulcanized rubbers, the adhesives of chlorosulfonated polyethylene was modified with the help of the products of aniline and glycidyl ester of methacrylic acid (Kablov et al. 2012).

Forty years ago, in the United States, a geomembrane was first developed as a roofing membrane and pond liner material made of chlorosulfonated polyethylene. In different regions of the world, geomembranes have been used as floating covers for the storage of municipal potable water and containment in industries. These chlorosulfonated polyethylene have proven to be a good choice of material as geomembranes. These floating covers are designed for the prevention of contamination and debris from infiltration to the reserved source of water (Fraser et al. 2019).

As Chlorosulfonated polyethylene possesses excellent resistance towards irradiation, heat, weathering, sunlight, and ozone, therefore, it is widely used as sheeting material for cable construction in various fields like in nuclear energy plants (Simendić 2017).

To find out the solution to problems related to the capping of steep slopes during the closure of hazardous waste piles and old municipal landfills, CSPE is considered an excellent material for geotextile and geocomposites. This product can overcome the problems related to surface friction and also has resistance towards puncture and localized subsidence. A sheet of chlorosulfonated polyethylene on lamination with a nonwoven geotextile either on one or both sides produces the desired product (Frobel and Taylor 1991).

### **3.6.2 Ecological Impacts**

In general, chlorosulfonated polyethylene is considered a safe material. Due to the presence of residual carbon tetrachloride ( $\text{CCl}_4$ ) and chloroform some acute or chronic potential health effects of chlorosulfonated polyethylene have been reported (DuPont 2007). This chemical can enter into the body either by breathing or through the skin, which may irritate skin, eye, nose, throat, lungs. In Some cases, it shows adverse effects on the liver, central nervous system, and kidneys also. If additives are used in the formulations of chlorosulfonated polyethylene for the purpose to enhance additional properties, then their selection should be done very carefully as these additives can cause harmful emissions at higher temperatures. Thermal decomposition and combustion of chlorosulfonated polyethylene can produce hydrochloric acid (HCl), sulfur dioxide, and carbon monoxide, which are highly toxic and irritant (Akovali 2012a, b).

## **3.7 Polychloroprene Rubber (CR)**

Polychloroprene is a synthetic material composed of polymerized chloroprene and is commonly known as chloroprene rubber (CR) or neoprene with CAS number 9010-98-4. Among all the vulcanized elastomers, the polychloroprene exhibits good performance. It has better resistance than natural rubber towards oils, water, solvents, and heat. At 20 °C the density of CR is 1.22–1.25 g/cm<sup>3</sup>, melting point is 40 °C, and

glass transition temperature  $-20\text{ }^{\circ}\text{C}$ . It is odorless, white to grey in color, its own remarkable mechanical and physical properties show resistance towards chemicals, acids, alkalis, sunlight, ozone, oil, heat, and fire. Polychloroprene never becomes soft on exposure to heat. Polychloroprene was discovered by Wallace Carothers and Julius Arthur Nieuwland in 1930. CR is considered to be a high demand product in the world market of elastomers (Wypych 2016).

Polychloroprene is an important diene-based elastomer, synthesized by free-radical emulsion polymerization from its monomer 2-chloro-1,3-butadiene which is known as chloroprene, (Campbell 2000). The monomer of polychloroprene is chloroprene, prepared by the reaction of dimerized acetylene with hydrochloric acid within a sealed system. In the presence of free radicals, formed monomer chloroprene is converted into polychloroprene polymer (PCP) by emulsion polymerization (Lynch 2001).

Polychloroprene can be vulcanized using metal oxides like zinc oxide and magnesium oxide. However, it can be vulcanized without metal oxides in the presence of zinc oxide. But to provide resistance, it is essential to add magnesium oxide (Coran 2013).

### 3.7.1 Applications

Polychloroprene has wide applications in different industries such as the automotive industry, construction industry, as adhesives and for missile launchers in the form of liner pads (Meier et al. 1971). The adhesive produced from polychloroprene is a solution type adhesive, made by the mixing of neoprene, anti-aging agent, magnesium oxide, filler and antioxidant. This adhesive can work in a wide range of temperatures from  $-50$  to  $+80\text{ }^{\circ}\text{C}$ , it possesses good resistance towards alcohol, oil, weak-acid, weak-alkali, aliphatic hydrocarbon, and water. It is commonly used for bonding structures or different materials. Polychloroprene on mixing with oil-soluble phenolic resins gives a better performance which can be applied to bind metals like steel, copper, aluminum, and nonmetals including ceramic, cement fiber boards, and plastics (Li 2011).

Polychloroprene has excellent mechanical properties, having good resistance towards tear, oil, weather, heat, chemical, ozone, and low flammability. These properties make it a choice next to nitrile rubber. Polychloroprene is widely used in various engineering applications like in the production of transmission/conveyor belts, gloves, as the material for gaskets, tubing, wraps and sheets, weather stripping, and hose (for gasoline), in cable coatings, as modifiers of bitumen, etc. Polychloroprene possesses low permeability to water which makes it suitable for sealer-type finishes used in masonry and concrete. Preformed chloroprene rubber joint seals are used for pavements of concrete (Akovali 2012a, b).

Polychloroprene is used as a raw material for contact adhesives, which are used for binding furniture, high-pressure laminates, kitchen cabinets, automotive trim,

custom display cabinets, roofing-membrane attachment, wall partitions, and interior and exterior panels (Akovali 2012a, b).

In many nuclear plants located in Foramark, Ringhals, and OKG chloroprene rubber is used in membrane valves to form membrane diaphragms. To control the flow of gas and water in power plants, membrane valves are used. (Rosato et al. 2004).

Neoprene fabrics are stretchable and thick enough to avoid wear and tear. Neoprene is a suitable material to be used for the manufacturing of wetsuits. The fabric made of neoprene has soft synthetic rubber foam which can be prepared thicker in comparison to other fabrics; therefore these wetsuits can provide heat insulation and protection from natural injury (Oh et al. 2019).

### 3.7.2 *Ecological Impacts*

Pure polychloroprene is not considered carcinogenic. All major polychloroprene are approved by the FDA. Whereas the processed form of polychloroprene may contain a variety of ingredients that are harmful and cause problems. Mainly chloroprene, toluene, and butadiene are volatile ingredients of polychloroprene along with thiourea and lead (Report on Carcinogens 2011).

The monomer chloroprene is a highly reactive and volatile material that is identified as carcinogenic to humans having 4.8 h as estimated residence time in the atmosphere. It is also supposed to be a strong toxicant to the neuro, endocrine, blood, and cardiovascular systems. Acute exposure affects the liver and kidneys also. Chloroprene is also identified as a toxic air contaminant. At low concentrations, the vapors of chloroprene cause irritation in the eyes and respiratory tract whereas at high levels these vapors affect central nervous system depressants.

EPA (An official website of the US Government) included Butadiene in the list of toxic pollutants. Butadiene is used in the manufacturing of polychloroprene. It was concluded from the study which was conducted at the EPA's Laboratory that during the processing of polychloroprene the emission levels of butadiene were 2–40% (US EPA 1985). Acute high-level exposure to butadiene may cause nausea, damage to the central nervous system, and lowering of the pulse whereas irritation of the throat, eye, and respiratory tract was caused by its low-level exposure. Other volatile ingredients like lead and thiourea compounds are already considered hazardous to human health. Lead and its compounds especially Lead oxide whether it is water-soluble or not, are poisonous in nature. Lead acts as a cumulative poison and is able to accumulate in soft tissues, the liver, and kidneys (Akovali 2007).

The small amount of rosin or colophony in polychloroprene adhesives is a skin contact sensitizer. It was stated by the EU that if the colophony level in polychloroprene is 0.1% or greater then it must be labeled as a potential skin contact sensitizer (EU Dangerous Preparations Directive 1999/45/EC 2002). On another side, polychloroprene shows very less oral toxicity, even if a person comes in direct contact or from gloves, clothing, boots, etc. This polymer is also responsible for producing



adverse effects in this way. Irritation and skin allergic reactions were reported due to unused thiourea left after vulcanization. The burning of polychloroprene liberates hydrogen chloride gas to the environment which is an irritant to the eye and respiratory tract. The chlorine content present in polychloroprene is also accountable for the release of dioxin throughout its lifecycle. This dioxin is a highly toxic chemical and carcinogenic to humans (IARC Group 1 carcinogen) (Akovali 2007).

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