CPE: A unique polymer for rubber and plastics extrusion

by Vijay Kotian and Nathan Groves, ARP Materials

Chlorinated polyethylene (CPE) polymers were developed by DuPont in the late 1950s by a simple chlorination of polyethylene (PE) in a solution process using a solvent. In 1971, Dow Chemical Company introduced Tyrin CPE using a more efficient and cost-effective aqueous suspension chlorination known as the slurry process (ref. 1). The polyethylene feedstock is in a powder form and the final CPE product remains in powder form. The chlorination process can be modified to produce amorphous (non-crystalline) products or products that contain residual crystallinity. The generalized chemical structure of CPE is shown in figure 1.

The ASTM D1418 designation for chlorinated polyethylene is CM, where C denotes chlorine and M denotes a saturated chain of polymethylene in the CPE polymer. The saturated backbone of CPE in figure 1 imparts excellent ozone, oxygen and heat resistance to the end product.

In the production process, the controlled variables include PE molecular weight, molecular weight distribution, chlorine content, residual crystallinity, rate and temperature of chlorination. By selectively controlling these variables and other process parameters, a number of different CPE resins and elastomers can be produced. All of these factors are important for the final characteristics of the polymer, i.e., physical properties, processing and chemical resistance.

Chlorine content

The chlorine content in CPE plays a significant role in determining the performance characteristics of the final product. Higher chlorine content will help improve oil, chemical and flame resistance, but will decrease the low temperature performance of the end product.

Current commercial grades of CPE contain 25-42% chlorine by weight. The 36% chlorine content grades with low residual crystallinity are used for rubber applications. The 25% chlorine content grades with high residual polyethylene crystallinity (higher heat of fusion) are generally targeted for thermoplastic applications.

Table 1 - Keliren CPE grades for wire and cable

Chlorine (%)	Mooney viscosity (ML 1+4) 121°C	Grade	Application
25	120 ± 5	CM 2535	Thermoplastic jacket and tubing
30	75 ± 5	CM 6530	Low temperature, specialty blends
36	80 ± 5	CM 3680	General purpose jacket
36	85 ± 5	CM 3685	General purpose jacket
36	100 ± 5	CM 3605	Higher performance jacket
42	80 ± 5	CM 422	Improved flame retardance and oil resistance

Molecular weight

The molecular weight and molecular weight distribution of polyethylene play key roles in determining the processing characteristics and physical property performance of the final product. The compounder can select the grade to achieve the best balance of processability and performance.

Processing

CPE as a primary thermoplastic resin can be calendered, injection molded or extruded. The finished products are tough, chemical and weather resistant, as well as flame resistant. The chlorine molecule on the polymer backbone gives a built-in ignition resistance.

CPE resins have extraordinary compatibility and processing ranges. They can be used as blends with PE, ABS, EVA, EPDM and polyolefin elastomers to enhance toughness, flame resistance, and oil and chemical resistance. As a modifier, CPE is widely used to enhance the impact properties of PVC products for pipe, siding, window profiles, fencing and other building and industrial applications.

CPE as a base elastomer requires the use of crosslinking systems other than conventional sulfur systems (ref. 2). The three widely used cure systems are peroxide, thiadiazole and electron beam radiation. It can be compounded for calendering, injection molding or extrusion.

CPE can also be blended with other elastomers, such as EPDM, CSM and NBR/PVC. It can be used to improve oil and flame resistance to these compounds.

Applications

CPE is widely used in an extrusion process for producing wire and cable, hose, tubing, foam and other products for building and industrial applications.

This article will only highlight wire and cable and hose rubber products, the two largest applications for CPE in North America.

Figure 1 - generalized chemical structure of chlorinated polyethylene (CPE)

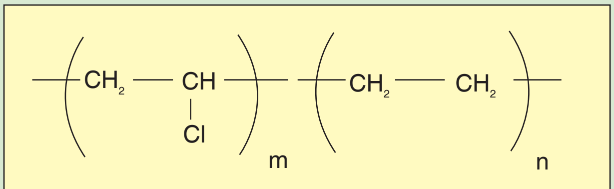

Table 2 - Keliren CPE in 105°C colorable heater cord	
Ingredient	*phr*
Keliren CM 3580	100
Calcium carbonate	60
Silica, precipitated	15
Magnesium oxide	5
TOTM	30
TMPTME	5
Irganox 1010	2
Antimony oxide	5
Vulcup 40KE	5
Property	*UL62, Class 47*
Tensile strength, psi/MPa	1,200/12.7 minimum
Elongation at break, %	200 minimum
Air oven aging, seven days at 136°C	80 minimum
Tensile strength, % retained	50 minimum
Elongation, % retained	60 minimum
IRM 902 oil aging, seven days at 136°C	60 minimum
Tensile strength, % retained	
Elongation, % retained	

Table 3 - Keliren CPE for extra heavy duty cable jacket	
Ingredient	*phr*
Keliren CM 3605/3610H	100
Magnesium oxide	5
Aluminum silicate, functionalized	40
Silica, precipitated	15
DINP	35
N550 black	2
Paraffin wax	2
SR-350	4
Vulcup 40KE	5
Property	*ICEA S-19-81 NEMA WC3*
Tensile strength, psi/MPa	2,400/16.5 minimum
200% modulus, psi/MPa	700/4.8 minimum
Elongation at break, %	300 minimum
Air oven aging, seven days at 100°C	70 minimum
Tensile strength, % retained	60 minimum
Elongation, % retained	
IRM 902 oil aging, 18 hours at 121°C	60 minimum
Tensile strength, % retained	60 minimum
Elongation, % retained	

Wire and cable

The most common grades of Keliren CPE for wire and cable applications are listed in table 1. CPE based compounds are approved for use in numerous wire and cable applications by the following specifying agencies: UL (Underwriters Laboratories); CSA (Canadian Standards Association); ICEA (Insulated Cable Engineers Association); NEMA (National Electrical Manufacturers Association); ASTM (American Society for Testing and Materials); IEEE (Institute of Electrical and Electronics Engineers); and MIL (United States Military Standard).

CPE based compounds listed in tables 2, 3 and 4 can be used as a benchmark to develop products that can meet the above listed standards and specifications (ref. 3). The selection of specific CPE grade, fillers, stabilizers, antioxidants and flame retardants, and the use of a wide range of polymers as blends in the end formulation may be necessary to meet some of the most stringent wire and cable specifications.

Table 4 - Keliren CPE thermoplastic jacket for cable, hose, tubing and profile	
Ingredient	*phr*
Keliren CM 2535	100
HDPE or LMDPE	30
DER-331	5
Carbon black, N550	35
Antimony oxide	10
Saytex 8010	10
Agerite MA	1
Paraffin wax	2
Property	*ICEA S-73-532*
Tensile strength, psi/MPa	1,400/9.6 minimum
200% modulus, psi/MPa	1,000/6.9 minimum
Elongation at break, %	150 minimum
Heat distortion at 121°C, %	25 maximum
Air oven aging, seven days at 121°C	
Tensile strength, % retained	85 minimum
Elongation, % retained	50 minimum
IRM 902 oil aging, 18 hours at 100°C	
Tensile strength, % retained	60 minimum
Elongation, % retained	60 minimum

Table 5 - Keliren CPE grades for hose

Chlorine (%)	*Mooney viscosity (ML 1+4) 121˚C*	*Grade*	*Application*
30	60 ± 5	CM 6530	Low temperature
36	50 ± 5	CM 352L FRS	Thiadiazole cure
36	80 ± 5	CM 3680	General purpose
36	85 ± 5	CM 3685P	General purpose
36	100 ± 5	CM 3605 FRS	Improved adhesion
36	100 ± 5	CM 3610	High performance

For insulation applications, the use of CPE polymers with low soda content, preferably below 25 ppm, is recommended. The moisture resistance and electrical properties of CPE compounds can also be improved by replacing magnesium oxide with epoxy type resin as an acid scavenger, and using hydrophobic calcined treated clays instead of calcium carbonate, silica and other hydrophilic fillers in the formulation (ref. 4).

Hose

The common grades of Keliren CPE for hose applications are listed in table 5.

CPE can be used as an alternate base polymer to replace nitrile, polychloroprene and chlorosulfonated polyethylene for standard hose cover applications where abrasion is not a concern. A 36% chlorine content CPE compound will meet the volume swell requirements for SAE J 517 and ISO 18752 test standards. Due to the CPE saturated backbone, there is no need

Table 6 - Keliren CPE thiadiazole cure compound for a non-marking hose cover

Ingredient	*phr*
Keliren CM 3680	100
Calcium carbonate	40
Silica	20
Carbon black, HAF	10
Aluminum trihydrate	10
Magnesium hydroxide	5
Magnesium oxide	5
DINP	35
Paraffin wax	3
TBAB	0.4
Thiadiazole	1.6
Sulfur	0.5
Property	*Value*
Durometer A	70 ± 5
Tensile strength, psi/MPa	1,500/10.3
Elongation, %	400

Table 7 - Keliren CPE peroxide cured compounds for hose

Ingredient	*phr*
Keliren CM 3680	100
Carbon black, N550	100
Magnesium oxide	5
Dioctyl Adipate	30
Paraffin wax	3
TMPTMA	2
TAC	2
DCP	5
Property	*Value*
Durometer A	70 ± 5
Tensile strength, psi/MPa	1,500/10.3
Elongation, %	400

to add expensive antioxidants and antiozonants in the formulation. The 36% chlorine CPE compound also meets -40°C cold bend test requirements. A thiadiazole cure for hose covers is generally preferred over a peroxide cure for improved abrasion resistance (ref. 5). The general recipe for a 70 durometer thiadiazole cured CPE is shown in table 6.

For higher temperature hose applications, a peroxide cured compound is recommended (table 7). For power steering applications, a peroxide cured CPE compound is superior to nitrile and polychloroprene due to its superior resistance to transmission fluid at elevated temperatures. For improved adhesion to reinforcement in hose, the FRS grades are recommended. The Keliren CM 352L FRS grade provides the best balance of processability, scorch resistance, shelf life and product performance.

In 2017, Arkema introduced an organic peroxide, Luperox Air XL80, for continuous extrusion and curing of EPDM, HNBR and other elastomers in a microwave/hot air tunnel and steam autoclave processes (ref. 6). The use of this novel peroxide overcomes the undercured and sticky surfaces due to inhibition of the crosslinking reaction by atmospheric oxygen using traditional organic peroxides.

Table 8 - Keliren CPE peroxide air cured compounds for hose, tubing and profiles

Ingredient	*phr*
Keliren CM 3680	100
Talc	40
Silica	20
Clay	35
Aluminum trihydrate	15
TOTM	45
TMPTMA	5
TAIC	2
Luperox Air XL80	10
Desiccant	5
Property	*Value*
Durometer A	70 ± 5
Tensile strength, psi/MPa	1,500/10.3
Elongation, %	400

For CPE, the user of Luperox Air XL80 would also help overcome shelf life, scorch and processability problems generally associated with thiadiazole cure systems. Another major advantage would be that Luperox XL80 is a higher temperature performance product compared to the thiadiazole cure. Table 8 is a starting point formulation using Luperox XL80 for hose, tubing and profile products using air or steam. Use of UV absorbers may be needed for natural and colored products to meet stringent outdoor weatherability requirements.

Conclusion

Chlorinated polyethylene is a very versatile and unique polymer that can be used for both rubber and plastic products. In addition, its excellent compatibility with other polymers enables compounders to develop unique, proprietary and cost-effective compounds that can meet a broad range of standards and specifications for cable, hose, profile and other continuous extrusion applications.

References

1. DuPont Dow Elastomers, Technical Bulletin, 1996.

2. L.E. Sollberger and C.B. Carpenter, "Chlorinated polyethylene elastomers: A comprehensive characterization," Rubber Division, ACS, Meeting, Toronto, Ontario, Canada. May 1974.

3. R. Laasko and U.I. Viadya, "An overview of Tyrin chlorinated polyethylene and Hypalon chlorosulfonated polyethylene in the wire and cable industry," Wire and Cable Focus, Philadelphia, PA, September 1996.

4. R.L. Lieux, U.S. Patent 5,274,013, Moisture Resistant Thermoset Cable Jacket, December 28, 1993.

5. W.H. Davis and J.H. Flynn, "Tyrin brand CPE thiadiazole cure system studies: Chemistry and dispersion," Rubber Division. ACS, Technical Meeting, April 1985.

6. L.H. Palys, W. Pavlek, A. Defrancisco and S. Sorbo, "Luperox Air organic peroxides: New peroxide systems for crosslinking EPDM in hot air," Rubber World, March 2019.