Development of Thin-Walled Halogen-Free Cable Insulation and Halogen-Free Fire-Resistant Low-Smoke Cable-Sheathing Compounds Based on Polyolefin Elastomer and Ethylene Vinyl Acetate Blends

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ABSTRACT: There is a growing interest in the use of polyolefins and their copolymer blends in cable industries. The present investigation deals with the development of thin-walled halogen-free cable insulation and thin-walled halogen-free fire-resistant low-smoke cable sheathing compounds based on polyolefin elastomer (Engage®) and ethylene vinyl acetate (EVA) blends. Blends of Engage (an ethylene octene copolymer) and EVA, varying in proportions, are prepared on a two-roll mixing mill at an elevated temperature. Physicomechanical, electrical, and the most important flame-retardant properties of the dicumyl peroxide/triallyl cyanurate cured blends have been basically studied. Properly compounded Engage-EVA blends are found to be excellent materials in cable industry for insulation as well as for sheathing compounds. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2839–2848, 2007

Key words: cable; ethylene–octene copolymer; ethylene vinylacetate; aluminum trihydrate; dicumyl peroxide; blends

INTRODUCTION

Polymer blends have played a significant role in the last few decades in revolutionizing polymer technology, leading to important and useful applications. The term ''polymer blend'' can be defined as a combination of two or more structurally different polymers or copolymers giving rise to materials with a range of properties, not delivered by any of the constituents. Thus, reasons for using blends include attainment of specific article performance, by improving the technical properties of the original polymers, by adjusting the processing characteristics and reducing the cost.[1–3] Polymer blends may be generally categorized into two main classes: immiscible and miscible blends. Immiscible blends are those, which exist in two different phases, e.g., rubber-toughened plastics. On the other hand, miscible blends are those, which exist in a single homogeneous phase and may exhibit different properties, which are uncommon to both of the pure components. Apart from these two, there is a third category of blends, often quoted as technologically compatible blends or alloys. The latter are those that exist in two or more different phases on microscale, but exhibit macroscopic properties similar to that of a single phase material.[1,2]

Polymer blends may also be classified into three types depending on the nature of polymers: plastic–plastic blends, plastic–rubber blends, and rubber–rubber blends.

Plastic–plastic blends

Plastic–plastic blends are promoted to combat certain disadvantages of one polymer with the help of another. For example, polycarbonate can be blended with acrylonitrile butadiene–styrene terpolymer (ABS) to improve its stress-cracking and chemical resistance properties. Similarly polyphenylene ether (PPE) can be blended with polyamides to improve its processability and impact strength. PPE-polystyrene (PS) blends are miscible and are commercially produced as Noryl®. Apart from these, there are a large number of blends, which is beyond the scope of discussion in this article.

Plastic–rubber blends

Plastic–rubber blends have gained considerable importance in recent years. In fact, plastic–rubber blends possess a unique position in the polymer blend family because of their thermoplastic elastomeric (TPE) nature, that is, the elastomer-like per-

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formance properties coupled with plastic-like processing characteristics. The recyclability of these TPEs has increased their commercial importance manifold. There is a detailed review on TPEs by Coran.[4] Thermoplastic elastomeric polyvinyl chloride (PVC)/epoxidized natural rubber (ENR) blends,[5] PVC/polychloroprene (CR) blend,[6] PVC/carboxylated nitrile rubber (XNBR) and PVC/nitrile rubber (NBR) blends,[7] and NR/polyethylene (PE) blends[8] have been studied by several researchers. Impact-modified plastics mainly consist of plastic–rubber blends.[9,10] Some other examples of this category are polypropylene (PP)/ethylene–propylene–diene rubber (EPDM) blends, used in automotives, EPDM-HDPE blends used as impact modifier, PVC-EVA blends used for building industry and so on.[1]

Rubber–rubber blends

Since the prospect of continued synthesis of new polymeric materials is limited, efforts are on with higher appreciation to develop rubber–rubber blends for diverse applications. Blends of NR/SBR, NR/BR, SBR/BR, NR/SBR/BR, NR/SBR/EPDM, and butyl rubber/EPDM are few examples of such blends. Automobile tire is the major application area of rubber–rubber blends.

The application of polymer blends in cable industries is also increasing day by day. The recent developments on thermoplastic elastomers for cable application is reviewed by Djiauw and Westbrook.[11] Blends of ethylene propylene rubber and chlorosulfonated polyethylene (CSP) have been characterized as useful cable insulants.[12] Blends of EPDM and PE have been used as insulation for ship cables.[13] Kinetics of shrinkage of cable insulation based on PE and PP used for heat shrinkable application have been reported by Vorob'ev et al.[14] CSP/EVA and PVC-NBR blends also find applications in cable industries. NR/CR blends are used in railway signaling and in X-ray tube supply cables. Blends of thermoplastic elastomers like PE/EPDM and PP/EPDM find wide applications in cable industries.[13] Polyethylene and EVA have special significance in cable engineering, because they can be crosslinked by means of organic peroxides or high-energy radiations. Hence, EVA/LDPE blends are also common in cable applications. Cable sheath compounds from blend of EVA and hydrogenated nitrile rubber (HNBR) for flame and oil resistance have been studied by Meisenheimer and Borngaesser.[15] Blends of functionalized polyolefins and PVC can be useful as low halogen, fire resistant, low smoke sheath compound.[16] Vulcanization behavior of EPDM/CR[17] and chlorinated polyethylene (CPE)/EVA-based[18] sheath compounds have been investigated.

Polyolefin elastomer (POE) is basically a copolymer of ethylene and *n*-octene, commercialized as Engage®. Du Pont Dow Elastomer LLC launched the polymer in 1996. Engage is manufactured by INSITE technology using a new type of Metallocene catalyst having constrained geometry. INSITE technology allows extraordinary control over polymer structure, properties, and rheology. These POEs are available in different grades, where octene level varies from 10 to 35%. The most important features of Engage is its good flex-fatigue resistance, lower density, improved release property at high comonomer content, good electrical property, good thermal stability, aging property, and easy processability.[19] Only a few researches have reported so far on the use of Engage-based polyblends for the cable industry.[20] Hence, there is ample scope for carrying out studies using Engage as one of the components in the blend for cable applications. This may open up new dimensions in this field.

Earlier blends of Engage and EVA in different proportions have been prepared and characterized by the authors.[20] This article deals with the development of an insulation compound as well a sheathing compound for cable applications based on these blends. The specifications for thin-walled halogen-free insulation compound are as follows: tensile strength $\geq$ 7 MPa, elongation at break $\geq$ 125%, hot set elongation < 100%, permanent set < 25%, volume resistivity > 10^{10} ohm cm, and % acid generation – nil. On the other hand, the criteria for developing thin-walled halogen-free fire-resistant low-smoke (FRLS) cable-sheathing compound for low voltage application up to 3–4 kV have been specified as: tensile strength $\geq$ 8 MPa, elongation at break $\geq$ 125%, tear strength $\geq$ 2.5 N/mm, hot set elongation < 100%, permanent set < 25%, limiting oxygen index > 30, smoke density rating < 20%, and % acid generation – nil. Thus the objective has been to achieve the specifications with the Engage/EVA blends.

EXPERIMENTAL

Materials

Ethylene–octene copolymer Engage-8452®, supplied by Bhimrajka Impex Ltd. (Kolkata, India), has a density of 0.875 g/cm³, Mooney viscosity (ML_{1+4} at 121°C) of 11.0, melt flow index (MFI) of 3.0 g/10 min.

Pilene-1202®, supplied by PIL, (Mumbai, India), has a chemical composition of ethylene vinyl acetate copolymer (12% vinyl acetate), MFI (g/10 min) of 2.0, and density of 0.931 g/cm³.

Pilene-2825®, supplied by PIL, having a chemical composition of ethylene vinyl acetate copolymer (28% vinyl acetate), MFI (g/10 min) of 25.0, density of 0.95 g/cm³.

Levaprene-450®, supplied by Bayer India Ltd. (Mumbai, India), has a chemical composition of ethylene vinyl acetate copolymer (45% vinyl acetate), Mooney viscosity (ML_{1+4} at 100°C) of 20 ± 4 and density of 0.99 g/cm^3.

Other ingredients used were Pilnox TDQ® (NOCIL) and mercapto benzoimidazole (MBI) (Bayer) as antioxidants, Rhenogran P-50® (Rhein-Chemie) as special hydrolytic stabilizer for EVA, stearic acid, zinc oxide, titanium dioxide (TiO$_2$), calcined clay, HAF-LS carbon black, and precipitated silica as filler, Sunpar 2280® as processing oil, vinyl silane as coupling agent, and paraffin wax and aluminum trihydrate (ATH) as flame retardants.

A combination of dicumyl peroxide (DCP-98%, Atochem) and triallyl cyanurate (TAC) were used as crosslinking agents.

Preparation of the blends and the test samples

Engage and EVA blends are prepared on a 150 mm × 300 mm size two-roll mixing mill with rolls maintained at a temperature of ∼ 100°C by means of steam heating, as per the formulations. The total time of mixing vary from 10 to 15 min. The tensile sheets and test samples were molded in a compression molding hydraulic press at a temperature of 160°C and a pressure of 10 MPa for the optimum cure times as determined by the Monsanto Rheometer R-100.

Testing procedure

Tensile and hardness test

Dumb-bell specimens were punched out of the tensile sheets and the tensile strength, modulus, and elongation at break have been determined using a Zwick UTM as per IS: 10810 (Part-7) (1984) at a grip separation rate of 500 mm/min at room temperature. Tear strength has also been determined in the same machine using Trouser test specimen as per IS: 10810 (Part-7) (1984) at a same speed. Hardness of the vulcanizates have been measured by a hardness tester (Shore A) as per ASTM D-2240-86.

Thermal aging of the samples have been carried out at 150°C for 10 days in an air-oven as per IS: 10810 (Part 11) (1984).

Hot set test

It covers a method for determination of hot set elongation and permanent set under load at a specified temperature of sheathing compounds of electrical cables. The main purpose of this test is to verify a satisfactory degree of crosslinking in the test material. It has been performed at (200 ± 3)°C, under a mechanical stress of 20 N/cm^2 in hot set apparatus as per IS: 10810 (Part 30) (1984).

After giving the gauge-mark (1 in.), the dumb-bell test piece has been allowed to suspend in the air-oven under a suitable weight attached to that. After 15 min in the oven at 200°C, the gauge-mark has been measured within 30 s after opening the door for the hot elongation. The weight has then been removed and the test-piece has been left to recover for 5 min at 200°C. Finally, the test-piece has been taken away from the oven and allowed to cool down slowly to ambient temperature after which the gauge-mark has been again measured for the determination of permanent set.

Load is calculated as follows:

$$Load = (A \times 20 \times 102) \text{ grams}$$

where A is the cross section area of the test-piece (cm^2).

Hence

$$\text{Hot set elongation (\%)} = (N - M)/M \times 100$$

and

$$\text{Permanent set (\%)} = (P - M)/M \times 100$$

where M is the initial gauge length, N is the gauge length after 15 min under load, and P is the gauge length at room temperature after test.

Electrical properties

Volume resistivity

Volume resistivity of the samples (dimension 10 × 10 cm^2) has been measured in a Hewlett–Packard 4329-A high resistance meter at room temperature (25°C) with an applied voltage of 500 V.

Volume resistivity has been calculated using the following formula and measured as per ASTM D-257-66.

$$\text{Volume resistivity (ohm cm)} = \frac{AR}{t}$$

where A is the area of upper electrode (19.6 cm^2), R is the resistance (in ohm) between upper and lower electrode, and t is the thickness (in cm) of the test specimen.

Dielectric constant or permittivity (ε')

The permittivity of a substance is defined as the ratio of the capacitance of a capacitor having a given material as its dielectric to the capacitance of the same capacitor having vacuum as the dielectric.

TABLE I
Control Formulation for Zero-Halogen Insulation Compound Based on Engage-EVA Blends with Variation in Amount of Calcined Clay (in phr)

Ingredients	Mix number		
	I-1	I-2	I-3
Engage	75.0	75.0	75.0
Pilene-1202	25.0	25.0	25.0
TDQ	1.5	1.5	1.5
Stearic acid	1.0	1.0	1.0
Zinc oxide	10.0	10.0	10.0
Calcined clay	30.0	50.0	70.0
Titanium dioxide	10.0	10.0	10.0
Paraffin wax	2.5	2.5	2.5
Vinyl silane	1.5	1.5	1.5
Sunpar-2280	12.0	12.0	12.0
DCP	2.5	2.5	2.5
TAC	1.0	1.0	1.0
Total	172.0	192.0	212.0
% Polymer	58.1	52.0	47.2

The capacitance was measured by a digital capacitance meter (model: Agronic-57) and then from that value, dielectric constant of the material has been calculated.

Oil resistance test

Oil resistance of the samples have been tested by immersing the samples in ASTM oil-type 2 at 100°C for 24 h and then by observing the percent variation in tensile strength and elongation at break of the swollen samples as per IS: 10810 (Part 13) (1984).

Smoke density test

It covers a laboratory procedure for measuring and observing the relative amount of smoke produced by the burning or decomposition of a test specimen. The measurements have been made in terms of loss of light transmission through collected standardized conditions. This test has been performed as per ASTM D-2843-81. The samples have been cut from the cured compounds having dimensions of $25 \times 25 \times 6$ mm^3. The samples have been kept on wire-mesh of the smoke-box of dimension $300 \times 300 \times 790$ mm^3 and has been burnt with 40 psi pressure of LPG.

Percentage of light absorbed by smoke present in smoke box has been noted down at the intervals of 15 s each up to a duration of 4 min and % absorbance versus time has been plotted. From the graph, the smoke density rating in % has been calculated using the following formula:

Smoke density rating (%)

$$= (\text{covered area}/\text{total area}) \times 100$$

Test for limiting oxygen index

This test has been carried out as per ASTM D-2863-81 at room temperature to get an idea about the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen, which would just support the flaming combustion.

To perform this test, samples of dimensions $7 \times 3 \times 100$ mm^3 have been cut from the molded sheet of compound and put in gas chamber, with nitrogen flowing through it at a rate of 100 cc/min. Percentage of oxygen and nitrogen has been varied according to the required percentage of oxygen in chamber and the sample has been ignited. According to the specification, fire should not propagate up to 2 in. of the sample or burn for 3 min. The corresponding oxygen percentage in the mixture has been taken as the value LOI. The temperature of gas chamber and

TABLE II
Formulation of the Mixes with Variation of DCP and TAC Doses in Engage-EVA Blends (in phr)

Ingredients	Mix number					
	I-4	I-2	I-5	I-6	I-7	I-8
Engage	75.0	75.0	75.0	75.0	75.0	75.0
Pilene-1202	25.0	25.0	25.0	25.0	25.0	25.0
TDQ	1.5	1.5	1.5	1.5	1.5	1.5
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0
Zinc oxide	10.0	10.0	10.0	10.0	10.0	10.0
Calcined clay	50.0	50.0	50.0	50.0	50.0	50.0
Titanium dioxide	10.0	10.0	10.0	10.0	10.0	10.0
Paraffin wax	2.5	2.5	2.5	2.5	2.5	2.5
Vinyl silane	1.5	1.5	1.5	1.5	1.5	1.5
Sunpar-2280	12.0	12.0	12.0	12.0	12.0	12.0
DCP	2.0	2.5	3.0	2.5	2.5	2.5
TAC	1.0	1.0	1.0	2.0	2.5	3.0
Total	191.5	192.0	192.5	193.0	193.5	194.0
% Polymer	52.2	52.0	52.0	51.8	51.7	51.5

TABLE III
Physicomechanical Properties of Insulation Compounds

Physical properties	Mix number							
	I-1	I-2	I-3	I-4	I-5	I-6	I-7	I-8
Tensile strength (MPa)	8.7	8.9	9.2	8.5	9.2	9.3	10.9	11.2
Elongation at break (%)	560	540	510	590	530	520	510	480
Modulus at 100 % (MPa)	1.6	1.7	2.0	1.6	1.8	2.5	3.4	4.2
Modulus at 200 % (MPa)	3.5	3.6	4.2	3.5	3.7	4.1	5.3	6.0
Tear strength (N/mm)	5.5	5.9	6.2	6.8	5.5	5.8	5.5	4.8
Hardness (Shore A)	80	82	84	81	82	83	84	84
Air-oven aging (150°C, 10 days)								
% Variation in tensile strength	+8	+7	+6	+9	+6	+5	+4	+7
% Variation in elongation at break	−10	−9	−8	−10	−8	−7	−6	−10
Hot set test (200°C, 15 min)								
Hot elongation (%)	30	28	26	40	25	22	15	10
Permanent set (%)	5	4	4	5	2	2	1	0

sample was not allowed to rise above ambient temperature.

$$\text{LOI (\%)} = ([O_2]/[N_2] + [O_2]) \times 100$$

where $[O_2]$ is the volumetric flow rate of oxygen (cm^3/s) and $[N_2]$ is the volumetric flow rate of nitrogen (cm^3/s).

The apparatus used for the determination of LOI was FTA flammability unit - Stanton Red Croft (model SR-FTA-710).

Temperature index determination

With the increasing temperature, the value of LOI decreases. At least three LOI have been measured at high temperature. Then temperature was plotted as a function of LOI to get a straight line. By extrapolating that straight line to 21% LOI (normal % of oxygen in atmosphere), temperature index has been determined.

Percent acid gas generation test

This test has been carried out as per IEC-754 (1). Approximately 1 g of sample has been heated in a furnace at 800°C for 20 min with an air-blow of 110 mL/min. After that, the acid gas liberated has been allowed to absorb by 300 mL of NaOH solution. Then the total volume of NaOH has been made up to 400 mL. Then 100 mL of test solution has been taken; 2 mL of concentrated HNO_3, followed by 20 mL of (N/10) $AgNO_3$ solution has been added to it. A white precipitate of AgCl has been appeared. The mixture has been then titrated with (N/10) ammonium thiocyanate solution using ferric ammonium sulfate as an indicator. Similar titration has also been carried out for black sample.

$$\text{\% Acid gas} = 3.65 \times (B - A)F \times (400/100)$$
$$\times (100/1000)/\text{weight of sample}$$

where A is the volume of ammonium thiocyanate required to titrate test solution, B is the volume of ammonium thiocyanate required for performing blank test, and F is the factor of ammonium thiocyanate solution.

Corrosivity test of combustion gases

This test has been performed as per IEC-754 (2). One milligram of sample has been heated at 900°C for 30 min and then the liberated combustion gases have been allowed to absorb by distilled water. After that the electrolytic conductance and the pH of the resulting solution have been determined by conductivity cell and pH-meter, respectively.

TABLE IV
Dielectric Properties of Insulation Compounds

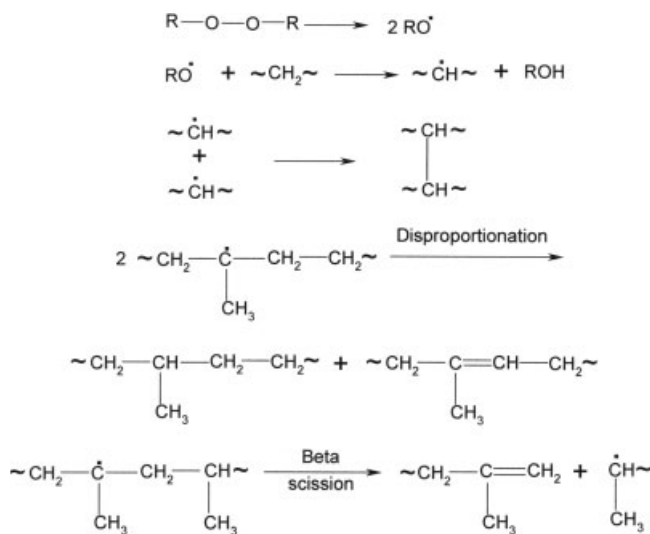| Electrical properties	Mix number							
	I-1	I-2	I-3	I-4	I-5	I-6	I-7	I-8
Volume resistivity (ohm cm)	5.78×10^{14}	5.61×10^{14}	5.52×10^{14}	5.49×10^{14}	6.81×10^{14}	1.12×10^{15}	3.11×10^{15}	5.33×10^{15}
Dielectric constant	3.01	3.06	3.12	3.10	2.83	2.7	2.51	2.49
Capacitance (pF)	37	39	42	35	30	31	28	26

Figure 1 Crosslinking mechanism of peroxide.

RESULTS AND DISCUSSION

Peroxides are very efficient crosslinking agents for saturated polyolefins as well as for saturated rubbers. The crosslinking chemistry using peroxide is well-known for years. The mechanism of peroxide crosslinking of polymer is less complicated as compared to sulfur vulcanization. In principle, the crosslinking process of high polymers by organic peroxides can be divided into three successive steps. A general scheme for the mechanism of action of a peroxide is shown in Figure 1. The first step is the homolytic decomposition of peroxide and generation of free radicals. This step is the rate-determining step (RDS) of the overall reaction. The second step is the abstraction of hydrogen atom from the polymer chain, resulting in stable peroxide decomposition products and polymer radicals. The final step consists of the combination of two polymer radicals to form a C—C crosslink. Sometimes, undesired side reactions like disproportionation or β-chain scission can also take place during the crosslinking process, as shown in Figure 1.

On the other hand, coagents are very reactive molecules that enhance the crosslinking efficiency of a peroxide significantly in case of saturated poly-

mers. TAC is a very common coagent, having three reactive allyl groups. In presence of DCP, it undergoes homopolymerization and cyclopolymerization creating multifunctional crosslinking sites.

It has been demonstrated earlier[20] that 25 : 75, 50 : 50, and 75 : 25 engage-EVA blends exhibit synergistic behavior in their tensile properties. This synergism is basically due to excellent compatibility between these two blend constituents, which could be interpreted due to their structural symmetry. It has also been found that 75 : 25 Engage-EVA blend gives the optimum combination of physical and electrical properties. Hence, 75 : 25 Engage-EVA blend was chosen for this study.

Insulation compound

An insulator acts as a barrier between conductor and surroundings or the sheath. This reduces the power losses and hazards of the energized conductor. The most important properties for cable insulation are:

a. Low dielectric constant
b. High dielectric strength
c. High insulation resistance
d. Low dielectric loss
e. Sufficiently low thermal conductivity
f. Preferably nonhygroscopic
g. Immunity to chemical attacks over a fairly wide range of temperature
h. Higher durability and longer life

The control formulation for developing zero-halogen insulation with Engage-EVA blends with variation in amounts of calcined clay from 30 to 70 phr is shown in Table I. On the other hand, formulations of the mixes with variation of DCP and TAC doses keeping the amount of calcined clay fixed at 50 phr are shown in Table II. Physicomechanical properties of insulation compounds (mix number I-1 to I-8) based on Engage-EVA blends are given in Table III. With increasing concentration of filler tensile strength, modulus, hardness, and tear strength increase, whereas elongation at break decreases. This is due to the semireinforcing nature of calcined clay implying

TABLE V
Fire-Resistant Properties of the Insulation Compounds

Fire properties	Mix number							
	I-1	I-2	I-3	I-4	I-5	I-6	I-7	I-8
Smoke density rating (%)	25	26	25	25	26	24	23	23
% Acid gas generation	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Corrosivity test								
pH	5.7	5.8	5.9	5.8	5.8	5.8	5.8	5.9
Electrolytic conductance (µs/cm)	61	62	62	62	62	62	62	62

TABLE VI
Formulations of the Mixes for Zero-Halogen FRLS Sheathing Compounds:
Variations of Engage-EVA Blend Ratios and Amounts of ATH (in phr)

Ingredients	Mix number					
	SH-1	SH-2	SH-3	SH-4	SH-5	SH-6
Engage	20.0	30.0	40.0	40.0	40.0	40.0
Pilene-2825	25.0	20.0	20.0	20.0	20.0	20.0
Levaprene-450	55.0	50.0	40.0	40.0	40.0	40.0
MBI	1.0	1.0	1.0	1.0	1.0	1.0
Rhenogran P-50	5.0	5.0	5.0	5.0	5.0	5.0
Ppt. silica	40.0	40.0	40.0	40.0	40.0	40.0
Vinyl silane	2.0	2.0	2.0	2.0	2.0	2.0
ATH	110.0	110.0	110.0	115.0	120.0	125.0
DCP	2.0	2.0	2.0	2.0	2.0	2.0
TAC	1.0	1.0	1.0	1.0	1.0	1.0
Total	261.0	261.0	261.0	266.0	271.0	276.0
% Polymer	38.3	38.3	38.3	37.6	36.9	36.2

that there is some sort of polymer–filler interaction. Calcined clay (50 phr) has been chosen as optimum filler concentration for pursuing further studies. Percent change of tensile strength and elongation at break after air-oven aging and hot set elongation decreases marginally with increasing filler loading. As the doses of DCP and TAC increase, tensile strength, modulus, and aging properties improve, whereas elongation at break, tear strength, hot set elongation, and permanent set decrease. This can be interpreted as the enhanced crosslink density of the blend-vulcanizate through cocuring of Engage and EVA in presence of DCP and TAC, leading to the formation of three-dimensional network structure containing stable C—C crosslinks. *In situ* graft-links formation between Engage and EVA could perhaps enhance the compatibility, which in turn also helps in cocuring. DCP (2.5 phr) and TAC (2.5 phr) have been chosen to be the best combination, as it imparts the optimum combination of physicomechanical pro-

perties. Table IV shows electrical properties of the insulation compounds (mix number I-1 to I-8). It has been observed that with the increasing dose of the filler (calcined clay), dielectric constant and capacitance increase but volume resistivity slightly decreases. This is due to the fact that the filler acts as a conducting medium because of its surface impurities. As the concentrations of DCP and TAC increase, volume resistivity increases but dielectric constant and capacitance decrease, which may be due to increased compactness of the medium as caused by the enhanced crosslink density and formation of three-dimensional network structure via DCP/TAC combination. This also helps in increasing the resistivity, indicating very good insulation property. Fire-resistant properties of the insulating compounds I-1 to I-8 are reported in Table V. It shows that there is no significant change in % acid gas generation, pH, and electrolytic conductance of mixes as one goes from I-1 to I-8. Thus it is concluded that I-7 mix for-

TABLE VII
Formulations of the Mixes for Zero-Halogen FRLS Sheathing Compounds:
Variations of Doses of DCP and TAC (in phr)

Ingredients	Mix number					
	SH-7	SH-8	SH-9	SH-10	SH-11	SH-12
Engage	40.0	40.0	40.0	40.0	40.0	40.0
Pilene-2825	20.0	20.0	20.0	20.0	20.0	20.0
Levaprene-450	40.0	40.0	40.0	40.0	40.0	40.0
MBI	1.0	1.0	1.0	1.0	1.0	1.0
Rhenogran P-50	5.0	5.0	5.0	5.0	5.0	5.0
Ppt. silica	30.0	30.0	30.0	30.0	30.0	30.0
HAF-LS	20.0	20.0	20.0	20.0	20.0	20.0
Vinyl silane	2.0	2.0	2.0	2.0	2.0	2.0
ATH	120.0	120.0	120.0	120.0	120.0	120.0
DCP	2.0	2.5	3.0	2.5	2.5	2.5
TAC	1.0	1.0	1.0	2.0	2.5	3.0
Total	281.0	281.5	282.0	282.5	283.0	283.5
% Polymer	35.6	35.5	35.4	35.4	35.3	35.3

TABLE VIII
Physicomechanical Properties of FRLS Sheath Compounds

Physical properties	Mix number					
	SH-1	SH-2	SH-3	SH-4	SH-5	SH-6
Tensile strength (MPa)	8.5	7.0	6.8	6.6	6.4	6.2
Elongation at break (%)	340	390	380	370	360	340
Modulus at 100 % (MPa)	2.0	1.8	1.5	1.5	1.6	1.7
Modulus at 200 % (MPa)	4.2	3.5	3.3	3.5	3.8	3.9
Tear strength (N/mm)	7.1	6.8	6.2	5.9	5.7	5.4
Hardness (Shore A)	81	81	81	82	84	86
Air-oven aging (150°C, 10 days)						
% Variation in tensile strength	+32	+30	+28	+29	+30	+30
% Variation in elongation at break	−39	−36	−33	−35	−35	−36
Oil resistance (in ASTM oil 2, 100°C, 24 h)						
% Variation in tensile strength	−25	−36	−43	−44	−46	−49
% Variation in elongation at break	−22	−30	−34	−30	−32	−36
Hot set test (200°C, 15 min)						
Hot elongation (%)	22	21	18	19	20	24
Permanent set (%)	2	2	2	2	2	2

mulation may be chosen as the best balance among the physicomechanical, dielectric, and flame retardancy properties for cable insulation compounds based on Engage-EVA blends.

From this study, the formulation described for I-7 has been selected as the optimum formulation for all physicomechanical properties as desired for insulation compound, which meets the specifications mentioned in the objective of the study.

FRLS sheathing compound sheath

Sheath or protective covering of a cable provides external protection and prevent the ingress of moisture, mechanical damage, chemical or electrochemical attack, and destruction by fire or any other harmful influences that are detrimental to the cable itself.

The sheath compound should have the following properties:

a. High mechanical properties to resist mechanical forces, vibrations, and shocks.
b. Good environmental resistance, e.g., (1) good oil and chemical resistance, (2) good ozone resistance, and (3) good flame and fire resistance.
c. High thermal stability.
d. Low emission of smoke, nontoxic, and noncorrosive gas in the event of fire hazards.

Table VI shows formulations of the mixes (SH-1 to SH-6) for zero-halogen FRLS sheathing compound with variation of Engage-EVA blend ratios and amounts of ATH. Conversely, mix formulations with variation in concentrations of DCP and TAC is shown in Table VII. Tables VIII and IX illustrate the physicome-

TABLE IX
Physicomechanical Properties of FRLS Sheath Compounds

Physical properties	Mix number					
	SH-7	SH-8	SH-9	SH-10	SH-11	SH-12
Tensile strength (MPa)	7.0	7.4	8.0	7.9	8.2	8.5
Elongation at break (%)	340	320	300	310	300	270
Modulus at 100% (MPa)	1.8	2.1	2.5	2.4	2.6	2.8
Modulus at 200% (MPa)	4.1	4.4	4.8	4.6	5.0	5.2
Tear strength (N/mm)	5.9	5.6	5.0	5.3	5.1	4.6
Hardness (Shore A)	84	84	84	85	86	86
Air-oven aging (150°C, 10 days)						
% Variation in tensile strength	+27	+24	+21	+23	+21	+24
% Variation in elongation at break	−33	−29	−26	−28	−23	−27
Oil resistance (in ASTM oil 2, 100°C, 24 h)						
% Variation in tensile strength	−44	−40	−30	−38	−30	−25
% Variation in elongation at break	−30	−28	−27	−28	−25	−20
Hot set test (200°C, 15 min)						
Hot elongation (%)	18	15	12	10	5	5
Permanent set (%)	2	2	1	1	0	0

TABLE X
Fire Properties of FRLS Sheath Compounds

Fire properties	Mix number					
	SH-1	SH-2	SH-3	SH-4	SH-5	SH-6
LOI	31.0	29.9	29.0	29.6	31.0	32.5
Smoke density rating (%)	7	7	7	6	5	3
Temperature index (°C)	335	331	318	320	328	332
% Acid gas generation	Nil	Nil	Nil	Nil	Nil	Nil
Corrosivity test						
pH	5.5	5.4	5.4	5.3	5.2	5.2
Electrolytic conductance (μs/cm)	63	62	62	63	63	63

chanical properties of all the formulations (SH-1 to SH-12). It is noticed that although SH-1 containing 55 phr of EVA (Levaprene-450) exhibits better physicomechanical properties, however, it is not economically feasible because of the higher cost of the Levaprene polymer. Therefore, the amount of Levaprene-450 needs to be reduced from 55 to 40 phr, as depicted in mix number SH-3, which consists relatively higher amount of Engage (40 phr). Therefore, the mix formulation SH-3 has been selected for further studies with the variation in amount of ATH. With increasing amount of ATH, the tensile strength, elongation at break, and tear strength decrease but modulus and hardness increase. This is because of the nonreinforcing nature of ATH. However, 120 phr of ATH (mix SH-5) has been chosen as the optimum proportion for obtaining best combination of all properties. On the other hand, as the doses of DCP and TAC increase, tensile strength, modulus, aging characteristics and oil resistance increase, but elongation at break, tear resistance, hot elongation and permanent set decrease. This can be attributed to the enhanced crosslinking density and cocrosslinking leading to the formation of a three-dimensional network structure. DCP (2.5 phr) and TAC (2.5 phr) have been chosen as the optimum combination of the blend of Engage and EVA in the proportion of 40 : 60.

Tables X and XI demonstrate the fire-resistant properties of FRLS sheathing compounds (mix number SH-1 to SH-12). From the tables, it is observed that as the amount of ATH increases, LOI and temperature index increases but smoke density-rating decreases indicating enhanced fire-resistant properties of the compound. This can be explained by the fact that ATH is an excellent flame-retardant and smoke-suppressant, which works via liberation of water molecules at high temperature creating thin impervious layer, so that oxygen cannot penetrate into the polymer matrix.

Therefore, SH-11 gives the optimum combination of physical, electrical, and fire-resistant properties required for zero-halogen FRLS sheathing compounds, which meets the given specifications.

In both the cases of insulation and FRLS sheath, % acid generation has been found to be nil, which satisfies the prime criterion for zero-halogen compound.

CONCLUSIONS

The following conclusions have been drawn from the present study.

Engage-EVA-12 blend (75 : 25) with 1.5 phr TDQ, 1.0 phr stearic acid, 10.0 phr ZnO, 50.0 phr calcined clay, 10.0 phr TiO_2, 2.5 phr paraffin wax, 1.5 phr vinyl silane, 12.0 phr Sunpar-2280, 2.5 phr DCP, and 2.5 phr TAC has been selected for optimum combination of all properties, which fulfill the best with the specifications for zero-halogen cable-insulation compound.

On the other hand, 40 : 20 : 40 Engage-EVA-28-EVA-45 blend with 1.0 phr MBI, 5.0 phr Rhenogran

TABLE XI
Fire Properties of FRLS Sheath Compounds

Fire properties	Mix number					
	SH-7	SH-8	SH-9	SH-10	SH-11	SH-12
LOI	31.8	31.8	31.9	31.9	32.0	32.0
Smoke density rating (%)	9	9	9	9	9	9
Temperature index (°C)	336	336	336	338	339	339
% Acid gas generation	Nil	Nil	Nil	Nil	Nil	Nil
Corrosivity test						
pH	5.2	5.2	5.1	5.1	5.1	5.1
Electrolytic conductance (μs/cm)	63	62	62	63	63	63

P-50, 30.0 phr ppt. Silica, 20.0 phr HAF-LS, 2.0 phr vinyl silane, 120.0 phr ATH, 2.5 phr DCP, and 2.5 phr TAC has been chosen for optimum combination of all properties, which matches best with the specifications for zero-halogen FRLS cable-sheathing compound.

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