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DEVELOPMENT AND CHARACTERIZATION OF SILANIZED EPDM/THERMOPLASTIC BLENDS FOR ENGINEERING APPLICATIONS

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A new terpolymer of vinyloxyaminosilane (VOS) grafted ethylene-propylene-diene terpolymer (EPDM) has been synthesized in a Haake Rheocord-90, torque rheometer. Grafting of VOS onto EPDM has been ascertained using FTIR spectra. Vinyloxyaminosilane grafted ethylene-propylene-diene terpolymer/polyvinyl chloride (EPDM-gVOS/PVC) and vinyloxyaminosilane grafted ethylene propylene diene terpolymer/linear low density polyethylene (EPDM-g-VOS/LLDPE) blends with different compositions were prepared using a two roll mixing mill. The mechanical and electrical properties of EPDM-g-VOS, EPDM-g-VOS/PVC and EPDM-g-VOS/LLDPE have been studied as per ASTM standards. Incorporation of silane moiety in to EPDM improves dielectric characteristics of EPDM. Further more the blending of silane grafted EPDM with thermoplastics like PVC and LLDPE enhances mechanical and electrical properties according to their nature and concentration and nature of crosslinks developed in their structure during curing. Data of mechanical and dielectric studies indicate that these products could be used as low and medium high voltage cable insulation for better performance than pure EPDM.

Keywords: Silane grafting, thermoplastic blends, mechanical properties, electrical properties, cable insulation.

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INTRODUCTION

Synthetic polymers in the form of blends and alloys find number of applications in the field of electrical insulation, as molded components and as extruded cables. Grafting of elastomer with silane moiety and subsequent blending with thermoplastics followed by curing leads to form a three dimensional network structure having adequate thermal endurance properties coupled with good dielectric and mechanical properties [1–5]. A good combination of flexibility and strength is an essential requirement of cable insulant. A continuous effort is being made to improve mechanical and thermal endurance properties of cable insulant without significant loss of dielectric characteristics.

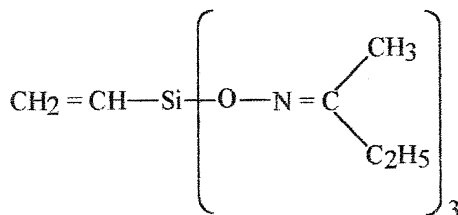
The blending of two or more polymers has gained considerable importance in recent years because the blends may give rise to certain properties, which can not be obtained by other means or from individual components [6–10]. However, blending requires compatibility of the polymer components involved. To improve the interfacial adhesion and compatibility, silanization can be used as an attractive method to enhance interaction between the immiscible polymer components [11–16].

In the present study, in order to develop EPDM compatible thermoplastic blends based on PVC and LLDPE, EPDM has been silanized using vinyloxyaminosilane by grafting technique. The resulting EPDM-g-VOS has been separately blended with varying compositions of PVC and LLDPE. The mechanical and electrical properties of blends of EPDM-g-VOS/PVC and EPDM-g-VOS/LLDPE have been studied to assess their utility for cable sheathing compounds for medium high voltage cables and for other engineering products.

EXPERIMENTAL

Materials

The EPDM (ENB) elastomer employed in this study was a commercial grade (Nordel IP 5750R) (ethylene/propylene/5-ethylidene-2-norbornene = 71/20/9 by wt.%, with Mooney viscosity, $ML_{(1+4)}$, of 50 at 125°C specific gravity of 0.88) of Du Pont Dow Elastomers, USA. The vinyloxyaminosilane (VOS) ($M_w = 313$, specific gravity = 0.988, viscosity = 11.5 cP and b.p. = 300°C) was procured from Wacker-Chemie, Germany. (Scheme I) LLDPE (ethylene-1-octene) used was commercial grade (Engage 8003) with Mooney viscosity, $ML_{(1+4)}$, of 22 at 121°C, MFI = 1.0 dg/min. and density = 0.880 g/cc. of Du Pont Dow Elastomers, USA. PVC marketed under the name Indavin with K-value 67 was obtained from IPCL, India. Dicumyl peroxide (DCP)



SCHEME I Chemical structure of vinyloxyaminosilane.

(99% assay with m.p. = 30°C) was obtained from Concord Chemical Industrial Co., Taiwan. Laboratory grade dibutyltin dilaurate (DBTDL), dibutyltin bis(lauryl mercaptide) (DBTBLM), dioctyl phthalate (DOP), calcium stearate, stearic acid, toluene, n-hexane and dimethyl formamide (DMF) were used as received.

Preparation of EPDM-g-VOS

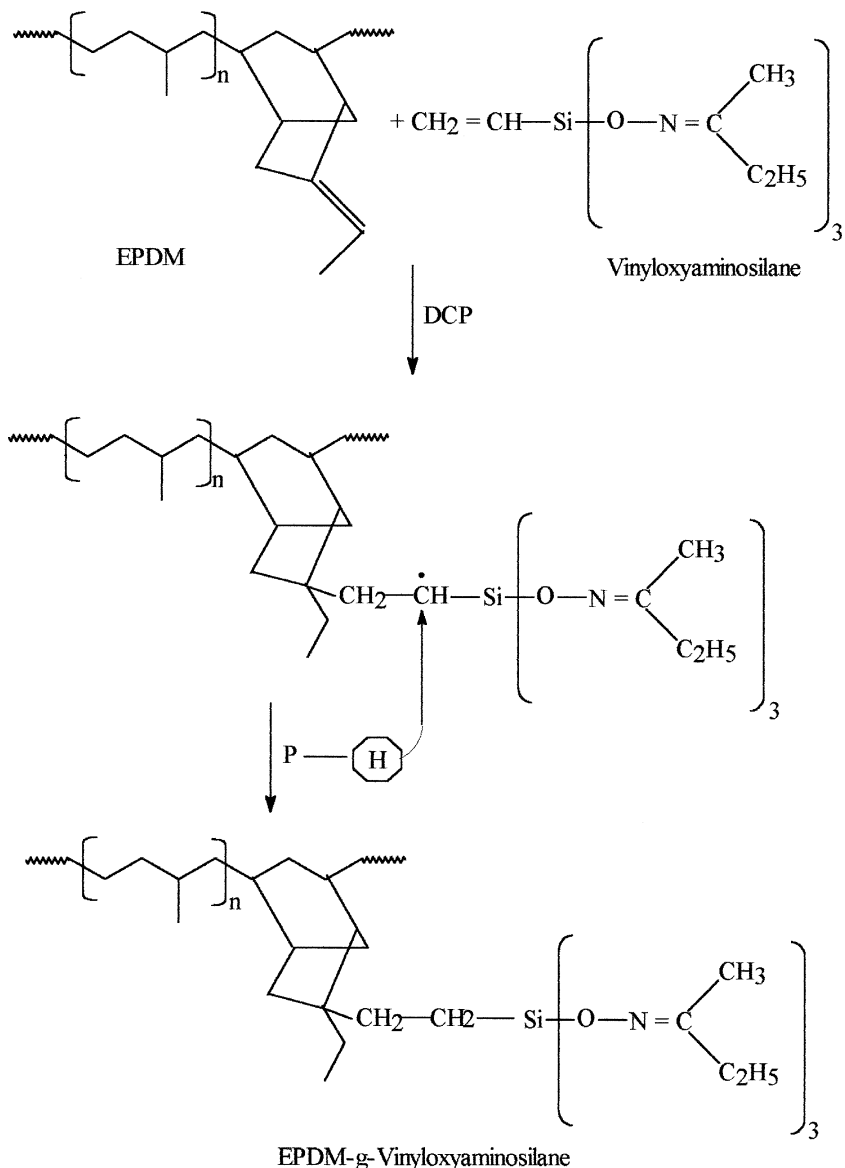
The EPDM-g-VOS has been synthesized in toluene (Table 1) using DCP as initiator, according to Scheme II. The grafting efficiency of VOS onto EPDM has been studied as a function of EPDM content, reaction time, reaction temperature and initiator concentration. Using the optimum efficiency conditions obtained from solution grafting, EPDM-g-VOS has been prepared by melt mixing technique. The EPDM (ENB) semi crystalline granules were coated with 0.2 wt.% dicumyl peroxide (DCP) initiator dissolved in 2.0 wt.% vinyloxyaminosilane (VOS). The treated elastomer was processed in a Haake Rheocord-90, torque rheometer at 160°C for 6 minutes at 30 rpm.

Preparation of EPDM-g-VOS/PVC Blends

The calculated amount of PVC (100 phr) with stearic acid (1.0 phr) and calcium stearate (1.5 phr) was charged in a high speed mixer

TABLE 1 Conditions of graft copolymerization

Condition	Description				
EPDM concentration (mole %)	10	15	20	25	30
VOS concentration (mole %)	1.0	1.5	2.0	2.5	3.0
Reaction time (hours)	3	5	7	10	—
Reaction temperature (°C)	150	160	170	180	—
Initiator concentration (mole %)	0.1	0.2	0.3	0.5	—
(based on the vinyl monomer)					



SCHEME II Schematic representation of grafting of vinyloxyaminosilane onto EPDM.

(Thyssen Henschel, model FM-10LB, Germany) at 3000 rpm for 5 minutes at 70°C. The stabilizer (DBTBLM, 3 phr) was then added and

TABLE 2 Nomenclature of blend compositions

Code	EPDM	PVC	LLDPE	EPDM-g-VOS
E	100	0	0	0
P	0	100	0	0
L	0	0	100	0
EV	0	0	0	100
EV ₁₀ P ₉₀	0	90	0	10
EV ₂₀ P ₈₀	0	80	0	20
EV ₃₀ P ₇₀	0	70	0	30
EV ₂₅ P ₇₅	0	0	75	25
EV ₅₀ P ₅₀	0	0	50	50
EV ₇₅ P ₂₅	0	0	25	75

thoroughly mixed at 90°C for 5 minutes. DOP (50 phr) was then slowly mixed for 10 minutes and then the temperature is gradually raised to 125°C to make good dispersion of additives with PVC resin. The total time taken for compounding plasticized PVC was 20 minutes.

The masticated EPDM-g-VOS and plasticized PVC were blended using DCP (2 phr) as curative in a two-roll mixing mill at 180°C for 20 minutes. The varying compositions of EPDM-g-VOS/PVC blends are presented in Table 2.

Molding

The blends were processed in the form of 3 mm sheets using compression molding technique at 180°C for 10 minutes using 100 kg/mm² pressure. The test specimens with required dimension were prepared from the compression-molded sheets using punching technique as per ASTM standards.

Preparation of EPDM-g-VOS/LLDPE Blends

The calculated amount of EPDM-g-VOS, 0.1 wt.% dibutyltin dilaurate (DBTDL) and fixed amount of DCP (1.0, 2.0 and 3.0 wt.%, based on the amount of EPDM-g-VOS) were preblended in a two-roll mixing mill at 80°C for 10 minutes. Blends of EPDM-g-VOS with LLDPE were prepared in a two-roll mixing mill (Nishimura 84.301 Type, Japan). The LLDPE was blended with EPDM-g-VOS with different concentrations of DCP in the molten state at 180°C for 15 minutes and the optimum level of initiator (DCP) concentration ascertained is about 2 mole%. The optimized compounding recipes of the blends are presented in Table 2.

Method of Sample Preparation

Test specimens for electrical studies were prepared using an electrically heated, compression molding machine with clamping pressure of 10 kg/cm^2 at 180°C for about 10 minutes. The compression-molded specimens of EPDM-g-VOS and EPDM-g-VOS/LLDPE were cured by immersing in boiling water for 2 hours.

Fourier-Transform Infrared Spectroscopy

The grafting reaction was confirmed by Fourier-transform infrared (FT-IR) (Nicolet, IMPACT-400) spectroscopy. The spectra for EPDM-g-VOS and EPDM-g-VOS/PVC and EPDM-g-VOS/LLDPE blends were obtained using compression-molded thin films.

Mechanical Properties

Tensile strength of the samples was done at $25 \pm 2^\circ\text{C}$ according to ASTM D 412-87 method using dumb bell shaped test pieces at a cross head speed of 500 mm/minute using an Universal Testing Machine (ZWICK-1484). The hardness of the samples was measured according to ASTM D 2240-86 and the results are expressed in Shore A units.

Volume and Surface Resistivities

The volume and surface resistivities of the molded specimens were measured as per ASTM D 257-83 using SIGMA MM 87, Million Mega Ohm Meter at 500 V for 60 seconds at room temperature. The diameter and thickness of the specimens were 100 mm and 4 mm respectively.

Dielectric Strength

Dielectric strength of the molded specimens (diameter 100 mm and thickness 4 mm) was measured according to ASTM D 149-87 using SHEARING BRIDGE, Vettiner, France (accuracy 0.08%) at 250 V and 50 Hz.

Dielectric Constant and Loss Factor

Dielectric constant and loss factor of specimens were measured as per ASTM D 149-87 using SHEARING BRIDGE, Vettiner, France (accuracy 0.08%) over the temperature range between 30°C and 150°C

at 50 Hz. The diameter and thickness of the specimens were 51 mm and 4 mm, respectively.

Arc Resistance

Arc resistance of the molded specimens (diameter 100 mm and thickness 4 mm) were measured according to ASTM D 495 using ARC RESISTANCE TESTER (Enamelled Wire Testing Equipments, Puna, India) at 250 V and 50 Hz.

RESULTS

Fourier-Transform Infrared Spectroscopy

EPDM-g-VOS

Figure 1 presents the FT-IR spectra of EPDM-g-VOS, EPDM-g-VOS/PVC and EPDM-g-VOS/LLDPE blend (E₇₅L₂₅). The IR spectrum of EPDM-g-VOS [Figure 1 (a)] reveals: -CH₂ rocking vibration at 1460 cm⁻¹ and -CH₃ symmetric bending vibration due to the propylene group at 1365 cm⁻¹. However C-H stretching vibration (vinyl) at 3265 cm⁻¹, C=C stretching vibration at 1663 cm⁻¹ and -CH₂-wagging vibration of Si-CH=CH₂ at 930 cm⁻¹ of VOS HAVE disappeared due to grafting of VOS with unsaturation or allylic positions present in the side chain of ENB of the EPDM. It is also noticed that the band intensity due to unsaturation (>C=CH-) present in the side chain of ENB content termonomer of EPDM at 815 cm⁻¹ is also decreased. However the Si-O stretching vibration at 1094 cm⁻¹ is not affected. These observations support the fact that >C=CH- is utilized for new chemical bond formation with VOS.

EPDM-g-VOS/PVC

FTIR spectrum of EPDM-g-VOS/PVC [Figure 1(b)] reveals the aliphatic C-H stretching vibration at 2926 cm⁻¹ and the C-Cl stretching vibration at 620 cm⁻¹.

EPDM-g-VOS/LLDPE

The FT-IR spectrum of crosslinked EPDM-g-VOS/LLDPE blend having composition E₇₅L₂₅ is presented in Figure 1 (c). The bands obtained are: -CH₂ rocking vibration at 1455 cm⁻¹, -CH₃ symmetric bending vibration at 1370 cm⁻¹ and -(CH₂)_n-wagging vibration at 730 cm⁻¹. A band at 1095 cm⁻¹ due Si-O stretching vibration clearly indicates the formation of -Si-O-Si- linkage in the blend.

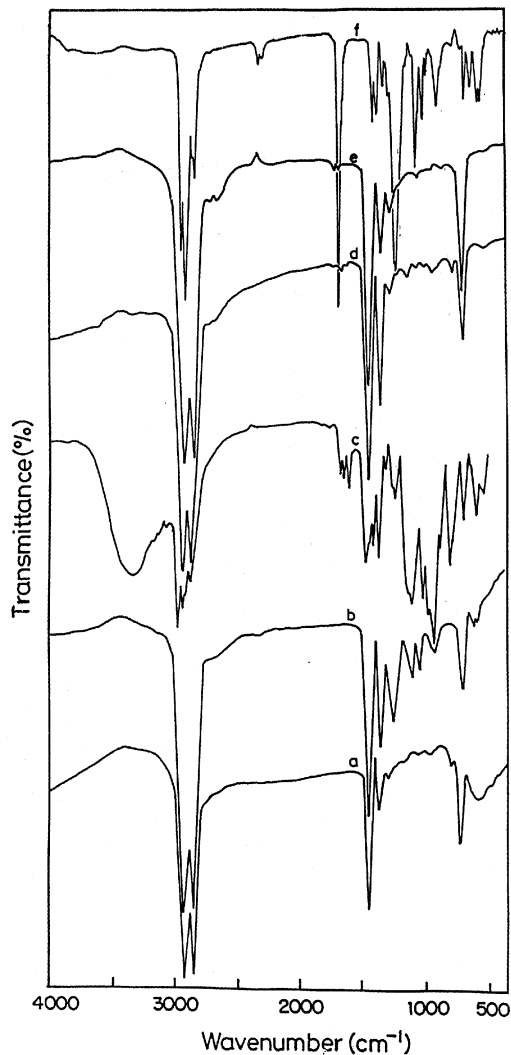


FIGURE 1 FT-IR spectra of a) EPDM-g-VOS, b) EPDM, c) VOS, d) LLDPE, e) EPDM-g-VOS/LLDPE and f) EPDM-g-VOS/PVC.

Mechanical Properties of EPDM-g-VOS

The mechanical properties of dicumyl peroxide crosslinked EPDM and hot water cured EPDM-g-VOS are presented in Table 3. It is observed that tensile strength, Young's modulus and hardness are decreased due to chain branching when VOS is grafted onto EPDM.

TABLE 3 Mechanical properties

Properties	EPDM	PVC	LLDPE	EPDM-g-VOS	EPDM-g-VOS/PVC*			EPDM-g-VOS/LLDPE*		
					*90%	*80%	*70%	*25%	*50%	*75%
Tensile strength (MPa)	19	10	14	14	13	10	8	15	16	18
Elongation at break (%)	260	280	700	280	310	420	550	340	360	380
Young's modulus (MPa)	24	12	26	19	18	18	17	20	21	26
Hardness (Shore A)	73	70	68	65	77	73	69	70	72	75

The reduction in tensile strength, Young's modulus and hardness are 24.1%, 22% and 11%, respectively. However, the elongation at break is increased by 6% due to high flexibility and free rotation imparted by Si-O linkages.

Mechanical Properties of EPDM-g-VOS/PVC Blends

Data obtained from mechanical studies indicate that the blending of PVC with EPDM-g-VOS alters the strength properties according to their concentration and compatibility. The highest values of tensile strength, Young's modulus, elongation at break and hardness are obtained in the case of blend having 90% PVC and 10% EPDM-g-VOS due to higher miscibility and better compatibility (Table 3) than other combinations of blends. For example the tensile strength of the blend is about 22% higher than that of plasticized PVC, 26% higher than that of EPDM and about 18% higher than that of EPDM-g-VOS. The improvement in mechanical properties may be explained due to the formation of semi interpenetrating network between grafted EPDM-g-VOS and PVC.

Mechanical Properties of EPDM-g-VOS/LLDPE Blends

The mechanical properties such as tensile strength, elongation at break and Young's modulus of cured EPDM-g-VOS/LLDPE blends with increase in LLDPE composition are presented in Table 3. In the case of crosslinked blends the value of tensile strength is increased with increase in concentration of LLDPE. The increase in value of tensile strength may be explained due to the influence of crystalline domains of LLDPE. Observations similar to tensile behaviour of EPDM-g-VOS/LLDPE blends are also noticed in the case of the values of Young's modulus and hardness (Table 3). The elongation at break (Table 3) increases with increase in LLDPE and decreases with increase in EPDM-g-VOS. This behavior may be explained due to the formation of hybrid plastoelastic structure comprising flexible and rigid domains (TPE).

Electrical Properties of Epdm-g-vos

The electrical properties of peroxide cured EPDM and hot water cured EPDM-g-VOS are presented in Table 4. The grafting of VOS onto EPDM increases the surface resistivity by 14%, volume resistivity by 42% and arc resistance by 8% above ungrafted EPDM. However, the

TABLE 4 Electrical properties

Electrical properties	EPDM	PVC	LLDPE	EPDM-g-VOS	EPDM-g-VOS/PVC*			EPDM-g-VOS/LLDPE*		
					*90 %	*80%	*70%	*25%	*50%	*75%
Volume resistivity $\times 10^{11}$ (Ohm.cm)	2.8	1.52×10^{11}	4.32×10^{15}	4.0	6.9	5.21	1.52	3.2	3.8	4.6
Surface resistivity $\times 10^{11}$ (Ohm)	4.5	5.20×10^{11}	1.67×10^{15}	5.2	1.3	4.6	8.9	5.6	7.2	8.6
Dielectric strength (kV/cm)	620	820	680	760	980	770	730	810	840	870
Dielectric constant	2.7	3.5	2.3	2.0	2.6	2.4	2.3	2.8	2.9	3.1
Loss factor	0.0035	0.0046	0.00044	0.0022	0.005	0.003	0.002	0.0004	0.0002	0.0001
Arc resistance (sec)	120	85	180	130	130	135	145	170	176	182

values of dielectric constant and loss factor are decreased by 25% and 37% respectively due to the inclusion of silane moiety.

Electrical Properties of EPDM-g-VOS/PVC

The results of dielectric strength, volume resistivity, surface resistivity and arc resistance are shown in Table 4. The result of dielectric strength reveals that the blend EV₁₀P₉₀ possesses higher value than other blends, because of increase in the weight percentage of EPDM-g-VOS which in turn enhances the polarity of the blend and thereby decreases the dielectric strength.

The value of volume resistivity is increased by the addition of EPDM-g-VOS, however the blends having beyond 10%PVC composition, viz., EV₈₀P₂₀ and EV₇₀P₃₀ shows decreases in value as a result of poor mixing. The values of volume and surface resistivities and arc resistance of PVC blends are improved with incorporation of EPDM-g-VOS as well as the miscibility of PVC with EPDM-g-VOS.

Electrical Properties of EPDM-g-VOS/LLDPE

The effect of LLDPE concentration on electrical properties of cross-linked EPDM-g-VOS, LLDPE and blends of EPDM-g-VOS/LLDPE measured at room temperature are presented in Table 4. The electrical properties such as volume resistivity, surface resistivity, dielectric strength and arc resistance are decreased with increase in concentration of LLDPE in the blends due to increase of crosslink density associated with non-polar olefinic character. It is also observed that for, every 25 wt.% increase of LLDPE in the blend, the values decrease of volume resistance by 20%, surface resistivity by 10%, dielectric strength by 12% and arc resistance by 7% respectively. However, dielectric constant and loss factors are increased by 17% and 23% respectively and this may be explained due to the inert hydrophobic nature imparted by LLDPE.

Dielectric Constant and Loss Factor

The variation of dielectric constant and loss factor over a temperature range between 30°C and 150°C were studied for EPDM-g-VOS, LLDPE and EPDM-g-VOS/LLDPE blends. Typical results are presented in Table 4. The value of dielectric constant decreases with increasing temperature and the decrease in the value varies according to the nature of blend compositions. For example, the slope values obtained for blends of compositions E₂₅L₇₅ and E₇₅L₂₅ are 0.01 and

0.004 respectively. A similar trend is also noticed in the case of effect of temperature on the values of loss factor.

CONCLUSION

EPDM-g-VOS graft terpolymer was synthesized by both solution polymerization and melt mixing techniques. The grafting of VOS onto EPDM and condensation of the silane side chains with the formation of stable Si-O-Si crosslinking in the presence of hot water have been confirmed from FT-IR spectra. The mechanical properties such as tensile strength, elongation at break, Young's modulus and hardness of EPDM-g-VOS, EPDM-g-VOS/PVC and EPDM-g-VOS/LLDPE blends were determined as per ASTM standards. It is inferred that the improvement of mechanical properties in the case of EPDM-g-VOS/PVC blends is based on its miscibility and compatibility, whereas in the case of blends of EPDM-g-VOS/LLDPE, the LLDPE component influences the mechanical properties according to its composition in the blend.

Among thermoplastics used in the present investigation to prepare blends, polar PVC is incompatible with non-polar EPDM due to poor miscibility and is made compatible with EPDM through grafting of VOS on EPDM. Among the different % composition of PVC used with EPDM-g-VOS, the blend with 10% PVC possesses better mechanical and electrical properties than other compositions due to higher miscibility. The non-polar nature of both EPDM and LLDPE makes them compatible in all proportions. However, LLDPE-rich blends exhibit better mechanical and electrical properties due to the influence of the crystalline nature and non-polar hydrophobic character imparted by the polyolefin molecules. Data from mechanical and electrical studies reveal that the blending of EPDM-g-VOS with thermoplastics like PVC and LLDPE improves strength and dielectric properties better than those of the individual components involved. Furthermore, it is suggested that these blends could be used as stable medium-high voltage cable insulation up to 35 kV.

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