Polymer Degradation and Stability 96 (2011) 2080–2087

Contents lists available at SciVerse ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Effects of organic–inorganic hybrid coatings on durability of cross-linked polyethylene

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A R T I C L E I N F O

Article history:
Received 27 July 2011
Received in revised form
21 September 2011
Accepted 29 September 2011
Available online 6 October 2011

Keywords:
Thermo-oxidation
XLPE
Organic–inorganic hybrid coatings
Nanocomposite
Electrical properties

A B S T R A C T

Cross-linked polyethylene (XLPE) films have been coated with nanostructured hybrid organic–inorganic coatings in order to improve their durability. For this purpose, bi- and mono-layer coatings containing different amount of silica and different organic polymers have been prepared through sol-gel reactions and applied to XLPE commercial films. The thermo-oxidative stability, electrical strength and conductivity of XLPE coated films have been investigated after ageing in air at temperatures above the on-service conditions, i.e. at 105 and 120 °C for 1900 and 600 h, respectively. The performed investigations (FT-IR, DSC, TGA and electrical properties) showed that all the coatings tested were able to strongly protect XLPE against oxidation, and that the coating with a PVOH/SiO_2 layer gave the best protection. The increase of thermal resistance induced by the coatings reflects on the electrical strength after ageing, which is higher for coated samples than for uncoated ones. Moreover, while ageing has only a slight effect on electrical conductivity in different coated samples, a strong increase of conductivity was observed after ageing for highly oxidated uncoated samples.

1. Introduction

Cross-linked polyethylene (XLPE) is probably one of the most extensively used materials for high voltage insulation [1–4]: it is designed to operate at quite high temperatures (about 90 °C in continuous, but higher temperatures can be tolerated for short periods of time), without changes in the geometry of the insulator. In these conditions, thermo-oxidation can be an important source of damage of XLPE properties [5–10]. Conventional ways to improve the thermo-oxidative stability of polymeric materials are the use of antioxidant additives [11,12] and/or nano-fillers [13–17]. In this last case, the increased thermal stability has been ascribed to reduced oxygen diffusion. However, for lamellar shaped nanophases [16] a preferred orientation must be achieved during processing to obtain a substantial decrease of permeability, a feature that complicates the technology of production. An alternative way to nano-fillers is represented by the use of hybrid nanostructured organic–inorganic coatings derived by sol-gel reactions that can be applied on polymer surface by different conventional techniques, such as spray- dip- or spin-coating [18–21], even onto complex geometries. This approach can also overcome the problem of antioxidant removal from the surface layer in outdoor applications, and possible interactions of nano-fillers with free radicals during crosslinking.

It has already been demonstrated that these hybrid coatings are able to behave as protective and functional coatings for polymeric substrates [20,22–24], and in particular to improve barrier properties to oxygen diffusion [25–29], combined with good mechanical properties and transparency [20–33]. In addition, they can be easily prepared by sol-gel curing, which can be carried out under mild conditions and that allows a quite versatile formulation of the coating, so that properties, including adhesion to the polymeric substrate, can be adjusted to any specific application. Following previous studies on other electrically insulating polymers [34,35], in this paper, the effects on the thermo-oxidative stability of hybrid coatings with different compositions has been investigated on XLPE films. The amount of inorganic phase (silica), the number of coating layers and the inclusion of poly(vinylalcohol) (PVOH) in the organic phase, a polymer which exhibits excellent resistance to oxygen permeation, have been considered in coating formulation. Coated and uncoated XLPE samples have been submitted to accelerated ageing (at 105 and 120 °C for 1900 and 600 h, respectively) and the effects of the thermal stresses on oxidation rate, electrical strength and conductivity have been investigated.

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0141-3910/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymdegradstab.2011.09.023

2. Experimental

2.1. Materials

XLPE films (150 µm thick) were derived from a 400 kV cable (Nexans, France); they have a melting temperature of about 107 °C, an original crystallinity degree of 30 wt% (calculated from differential scanning calorimetry assuming an enthalpy of fusion of 280.0 J/g [36]) and a gel fraction of 70% (after decahydronaphthalene extraction [37]).

High purity tetraethoxysilane (TEOS, Aldrich), 3-isocyanatopropyltriethoxysylane (ICPTES, Fluka), ethanol (EtOH, Carlo Erba), tetrahydrofuran (THF, Sigma–Aldrich), hydrochloric acid 37% solution (Sigma–Aldrich), polyvinyl alcohol (PVOH, Fluka, with $M_w \approx 31{,}000$ and degree of hydrolysis 86.7–88.7%) and monohydroxy terminated polyethylene-block-poly(ethylene glycol) copolymer with $M_n \approx 2250$ g/mol containing 80 wt% of ethylene oxide (PE-PEG, Aldrich) were used as received without further purification.

2.2. Coatings preparation and deposition

Triethoxysilane-terminated polyethylene-poly(ethylene glycol) (PE-PEGSi) was prepared by the bulk reaction of monohydroxy terminated polyethylene-block-poly(ethylene glycol) copolymer with ICPTES as already reported in a previous paper [32]. All the hybrid coatings were prepared through sol-gel method from solutions containing TEOS, as the inorganic network precursor and PE-PEGSi or PVOH, as organic components, as described in details elsewhere [28,34].

Coated XLPE films have been obtained through the deposition, on both sides of the film (8.0 × 8.0 cm), of the sol-gel solutions by the spin-coating technique using a spin rate of 1000 rpm for 30 s. All coated films were obtained using XLPE films without any previous surface treatment except washing in methanol just before coating application. After the first spin-coater deposition the coated films were subjected to a thermal treatment at 60 °C in an air-circulating oven. Bi-layered coatings were prepared by applying a second coating layer (again on both film sides) on previously coated films using the same deposition procedure described above. At the end of depositions all the coated films were subjected to a final thermal post-treatment at 60 °C for 24 h in an air-circulating oven.

Four different types of coatings were prepared and investigated: i) COAT1: mono-layer consisting of PE-PEG/SiO_2 with an organic–inorganic weight ratio of 50:50; ii) COAT2: bi-layer with both layers having the same composition of COAT1; iii) COAT3: bi-layer; the layer in contact with XLPE has the same composition of COAT1 while the second one consists of PVOH/SiO_2 with an organic–inorganic weight ratio of 50:50; iv) COAT4: bi-layer, the layer in contact with XLPE has the same composition of COAT1 while the second one consists of silica derived from sol-gel reaction of TEOS.

Table 1
Composition and thickness of organic–inorganic hybrid coatings.

Coated-film code	Composition of the first layer[a]	Composition of the second layer[a]	Coating thickness[b] (µm)
COAT1	PE-PEG/SiO_2 50:50	–	0.6–0.7
COAT2	PE-PEG/SiO_2 50:50	PE-PEG/SiO_2 50:50	1.3–1.5
COAT3	PE-PEG/SiO_2 50:50	PVOH/SiO_2 50:50	1.3–1.5
COAT4	PE-PEG/SiO_2 50:50	SiO_2	1.3–1.5

[a] Organic–inorganic nominal weight ratio calculated assuming the completion of hydrolysis and condensation reactions of alkoxy silane groups involved in the sol-gel process.
[b] From the cross-sectional view of SEM pictures.

Coating thickness has been measured by scanning electron microscopy and the results are reported in Table 1.

2.3. Thermo-oxidation

Coated and uncoated XLPE films (8.0 × 8.0 cm) have been aged at 105 and 120 °C in a temperature controlled ventilated oven (air flow rate: 0.4 l/min) up to 1900 and 600 h, respectively. According to the DSC results, only a small fraction of the crystalline phase is melted at 105 °C, while melting is complete at 120 °C.

2.4. Thermal analysis

Aged and virgin samples have been submitted to thermogravimetric analysis (TGA) by means of a Q50 model (TA Instruments). A heating rate of 20 °C/min in nitrogen atmosphere was applied from 40 to 650 °C. Crystallinity has been investigated by means of differential scanning calorimetry DSC (Q10 model, TA Instruments) from 25 to 140 °C in nitrogen atmosphere and heating rate of 10 °C/min.

2.5. FT-IR spectroscopy

FT-IR spectra of aged and unaged XLPE films were obtained by an Avatar 330 (Thermo-Nicolet) instrument with a resolution of 4 cm^{-1} in transmission and in ATR (Attenuated Total Reflection) mode. In ATR mode a crystal of ZnSe (refractive index 2.4 at 1700 cm^{-1}) and a minimum or 256 scans were used in order to obtain a high signal-to-noise ratio. IR spectra were recorded on samples derived by the coated ones after removal of the external coating by a suitably slight abrasion with a razor blade.

The oxidation index, *O.I.*, has been calculated by the ratio of 1717 to 2022 cm^{-1} and 1717 to 1467 cm^{-1} absorbance peaks, from transmission spectra, and by the ratio of 1717 to 1467 cm^{-1} peaks, from ATR spectra [38–43]. For PE samples, both peaks at 2022 cm^{-1} and 1467 cm^{-1} correspond to the methylene vibration of polyethylene chain, which are not sensitive to oxidation, and therefore can be used as internal standard peaks for quantitative evaluations.

The percentage increase of *O.I.* ($\Delta O.I.$ %) due to thermal-oxidation of XLPE films has been calculated as:

$$\Delta O.I.\% = \frac{(O.I.)_{aged} - (O.I.)_{unaged}}{(O.I.)_{unaged}} \cdot 100 \quad (1)$$

2.6. Electrical strength measurements

Electrical strength was determined on a. c. conditions according to ASTM D 149 by means of two stainless steel electrodes, one spherical (Rogowsky type) with 15 mm diameter, and the other flat. The whole measuring equipment was immersed in silicone oil at room temperature during the measurements. Voltage was applied at an increasing rate of 30 kV/min at a frequency of 50 Hz. At least five measurements were performed for each sample. Results have been treated according to Weibull analysis [35].

2.7. Electrical conductivity

Dc volume conductivity was determined according to ASTM D257 with a three terminal configuration. Electrodes were deposited by gold evaporation under vacuum. A 10 kV/mm electrical field was applied by means of a Keithley 248 High Voltage Supply in nitrogen atmosphere at 90 °C, and the current flowing trough the electrodes was recorded by means of a Keithley Model 6514 Electrometer, up to 600 s after voltage supply. Conductivity was