



Improvement of the thermo-oxidative stability of low-density polyethylene films by organic–inorganic hybrid coatings

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ABSTRACT

LDPE films have been coated with single or bi-layer hybrid coatings formed through sol–gel reactions in order to improve their thermo-oxidative resistance. Different chemical compositions of the coating were investigated which differ either in the amount of the inorganic phase (silica deriving from tetraethoxysilane) or in the organic component (either alkoxy silane functionalized polyethylene–poly(ethylene glycol) diblock copolymers or poly(vinyl alcohol)). The thermo-oxidative stability of the coated films thus obtained has been assessed by means of isothermal differential scanning calorimetry (DSC) and isothermal thermo-gravimetric analysis (TGA) under accelerated conditions, i.e. at high temperatures in pure oxygen flow. Conventional ageing in air at lower temperature, slightly above the in-service one, has also been carried out. The obtained data show: a) a general improvement of the thermal-resistance for the coated LDPE samples; b) a particularly high thermal-resistance for LDPE coated with a bi-layer coating with pure silica in the top layer; c) the effectiveness of the accelerated techniques in qualitatively assessing the thermo-oxidative resistance of the coated polymeric systems.

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1. Introduction

Thermo-oxidation is one of the most important stresses that polyolefins (LDPE, HDPE, XLPE and PP) have to undergo during their lifetime [1–7]. The degradation of these materials has been extensively investigated [8–13] and the main ways proposed to improve their thermo-oxidation stability rely either on the use of additives or on the inclusion of nano-fillers in the bulk materials [14,15]. In this last case, the increased thermal stability has been ascribed to a reduced oxygen diffusion. A similar effect can in principle be obtained by the application of a nano-structured organic–inorganic hybrid coating [16–23], when it can provide a barrier towards diffusion of gases and low molecular weight products [24–27]. Indeed, the reduced permeability to oxygen for LDPE films coated with hybrid coatings has already been proved [28,29], as well as the increase in thermo-oxidative stability [30], and this paper is an extension of these previous studies.

Starting from the idea that a higher barrier to oxygen diffusion can give an improvement to oxidation resistance, mono and bi-layer hybrid coatings, based on silica as inorganic phase (generated from TEOS via sol–gel reactions) and containing organic phases

consisting of PVOH and/or trialkoxysilane terminated PE–PEG block copolymer, were tested on LDPE films. Ageing tests were carried out on coated and uncoated solid films under different test conditions: at a temperature just above the on-service conditions over long times and under accelerated conditions, at temperatures well above the LDPE melting temperature and under oxygen flow, according to well established procedures [31–36].

Extrapolation of accelerated tests to lower temperatures is not an obvious task, in particular when important thermal transitions occur at the increased temperatures. Therefore, a comparison of the results recorded under different conditions (accelerated tests and service temperature) is reported and discussed.

2. Experimental

2.1. Materials

LDPE thin films (50 μm thick) with a melting point of 102 °C and a crystalline weight fraction of 0.24, (determined by DSC under nitrogen atmosphere at a heating rate of 10 °C/min and assuming an enthalpy of fusion of 293.1 J/g for the 100% crystalline material [37]) has been used as the substrate.

High purity tetraethoxysilane (TEOS, Aldrich), 3-isocyanatopropyltriethoxysilane (ICPTES, Fluka), ethanol (EtOH, Carlo

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Erba), tetrahydrofuran (THF, Sigma–Aldrich), hydrochloric acid 37% solution (Sigma–Aldrich), polyvinyl alcohol with $M_w \approx 31,000$, degree of hydrolysis 86.7–88.7% (PVOH, Fluka) 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. Preparation of triethoxysilane-terminated copolymer

Triethoxysilane-terminated polyethylene-poly(ethylene glycol) (PE–PEGSi in the following) was prepared by the bulk reaction of monohydroxy terminated polyethylene-block-poly(ethylene glycol) copolymer with ICPTES (molar ratio of 1/1.1). The reaction was carried out in a 50 ml glass flask equipped with a calcium chloride trap and under magnetic stirring at 120 °C for 3 h, as already reported in a previous paper [21].

2.3. Preparation of single-layer hybrid coatings

Single-layer hybrid coatings, with different organic/inorganic ratios, were prepared and applied onto both sides of LDPE films according to the procedure elsewhere described [21,28,29]. Briefly, TEOS and PE–PEGSi were dissolved in warm THF under magnetic stirring at the concentration of 25% wt/v. Water (to promote the hydrolysis reaction), EtOH (to make the system miscible) and HCl (as catalyst) were added at the following molar ratios with respect to the overall ethoxide groups (deriving both from TEOS and functionalized copolymers): EtO–:H₂O:EtOH:HCl = 1:1:1:0.05 and finally partially cured in a closed vial at 60 °C for 2 h. At the end of the thermal treatment, the solution was deposited onto the LDPE (10–10 cm) by spin-coating using a spin rate of 1000 rpm for 30 s for each side of the films. The coated films were subjected to a thermal treatment at 60 °C for 2 h after the first-side deposition and a final post-treatment at 60 °C for 24 h in an air-circulating oven after a second deposition on the opposite side. All coated films were obtained using LDPE films without any previous surface treatment except washing in methanol before coating application.

Spin-coating was used to apply the coating to LDPE films, as it can allow to obtain very thin layers (typically 100–1000 nm) and it is known able to lead to uniform thickness over wide surface area, thus making the subsequent measurements more reliable.

2.4. Preparation of multilayer hybrid coatings

Multilayer coatings were prepared by applying (on both sides of LDPE film) a first coating layer containing PE–PEGSi and SiO₂, to ensure adhesion, and a second layer consisting of polyvinyl alcohol PVOH and SiO₂ or pure SiO₂; in all cases silica was generated from TEOS via sol–gel reaction. The first layer was prepared and applied as reported above for the single-layer coatings, while an EtOH/H₂O (1:1 v/v) solvent was used for the preparation of the solutions containing TEOS and PVOH. Before the spin-coater deposition of the second layer, the PE–PEG/SiO₂ coated films were thermally treated in an air-circulating oven at 60 °C for 30 min. A second coating layer on both film sides was then applied to the previously coated films, using the deposition procedure described above. After the second layer was applied, samples were subjected to a final thermal post-treatment at 60 °C for 24 h in an air-circulating oven.

Four different types of coatings systems were prepared and investigated: i) MONO-1, which consists of a single layer of PE–PEGSi and SiO₂ with an organic–inorganic weight ratio 33:67; ii) MONO-2, which consists of a single layer of PE–PEGSi and SiO₂ with an organic–inorganic weight ratio 67:33; iii) BI-1, a bi-layer coating consisting of a first layer of PE–PEG/SiO₂ 67:33 and

a second one of PVOH/SiO₂ with organic–inorganic weight ratio 50:50; iv) BI-2, a bi-layer coating consisting of a first layer of PE–PEGSi and SiO₂ 33:67 and a second one formed by net SiO₂ generated from TEOS via acid catalyzed sol–gel reactions. Composition, code and the thickness of the prepared coatings are reported in Table 1.

2.5. Ageing tests on solid films

Coated and uncoated LDPE samples were aged at 95 °C in a temperature controlled ventilated oven (air flow rate: 0.4 l/min). Three samples (size 50 × 50 mm) for each composition were aged and their weight recorded up to about 900 h. Beyond this time, uncoated LDPE samples were brittle and started losing small film fragments.

2.6. High temperature tests

The thermo-oxidative stability was evaluated under isothermal conditions by thermo-gravimetric analysis, TGA (Q50, Thermal Analysis), and differential scanning calorimetry, DSC (Q10, Thermal Analysis) in oxygen flow (60 mL/min). The investigated temperatures range from 150 to 170 °C in both experiments. Samples in the form of disks of 6 mm diameter and about 2 mg were heated from room temperature to the selected test temperature under nitrogen flow at a heating rate of 15 °C/min, before switching the gas to pure oxygen. As to what concerns DSC tests, the oxidative reactions generate an exothermic peak in the isothermal thermogram that can be characterized by the Oxidative Inflection Time (OIT) [31,32], determined at the end of the initial induction period, when the heat flow signal starts deviating from the original baseline, or by the Oxidation Maximum Time (OMT), i.e. the time at which the maximum of the peak is reached. For TGA test performed on polyolefins, previous studies [33,34] underlined the presence of a maximum at relatively short times in the isothermal thermogram, related to the formation of peroxides, and the possible use of the time to the maximum for the calculation of the apparent activation energy of the degradation process. Both OMT (DSC) and the time-to-maximum (TGA) were used to test the thermo-oxidative stability of coated and uncoated LDPE samples. Three samples were investigated for each system at all temperatures.

Moreover, virgin and aged (85 °C, 850 h) samples were submitted to scanning TGA test. In these experiments samples of about 2 mg in the form of disks (6 mm diameter) were heated at 15 °C/min from 30 °C to 650 °C in nitrogen flow.

3. Results

3.1. Preparation and characterization of coated films

Oxidation is the main responsible of failure of polyethylene items in electrical applications [38,39] and any treatment able to

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
MONO-1	PE-PEG/SiO ₂ 33:67	–	1.1 ± 0.3
MONO-2	PE-PEG/SiO ₂ 67:33	–	1.0 ± 0.4
BI-1	PE-PEG/SiO ₂ 67:33	PVOH/SiO ₂ 50:50	1.6 ± 0.3
BI-2	PE-PEG/SiO ₂ 33:67	SiO ₂	2.0 ± 0.5

^a x:y represents the nominal weight ratio of the organic and inorganic components assuming the completion of the hydrolysis and condensation reactions of alkoxy silane groups involved in the sol–gel process.

^b From the cross-sectional view of SEM pictures.

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