



Effects of coating composition and surface pre-treatment on the adhesion of organic–inorganic hybrid coatings to low density polyethylene (LDPE) films

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ABSTRACT

Organic–inorganic hybrid coatings, obtained through the sol–gel chemistry from tetraethoxysilane and polyethylene–poly(ethylene glycol) block copolymer, have been prepared in different compositions and applied to untreated and plasma treated LDPE films by spin coating. The mechanical properties of the coatings and the adhesion between coating and substrate have been characterized by fragmentation test. An increase in coating strength, elongation at break and adhesion has been observed with increasing the organic fraction in the hybrid coating. A plasma treatment of the LDPE surface, just before the application of the coating, lead to an increase of the adhesion between coating and substrate (interfacial shear strength), leaving almost unaffected coating strength and strain at fragmentation onset.

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1. Introduction

For many applications, surface properties of plastics do not fit the project requirements, due for instance to poor scratch and solvent resistance, lack of biocompatibility, etc. In order to improve surface properties and/or to add specific functionalities, such as for instance barrier against gas diffusion, antibacterial properties, UV resistance, etc., one possible approach is to apply a thin layer of a functional coating to the surface of plastics.

Many technologies can be used to apply a thin coating layer onto a plastic substrate, namely: physical vapour deposition (PVD) [1], chemical vapour deposition (CVD) [2,3] and chemical solution deposition (CSD). Among the CSD methods the sol–gel approach [4,5] seems particularly interesting, as it allows to prepare hard coatings in a wide

range of compositions, ranging from fully inorganic to nanostructured hybrid organic–inorganic materials [6–8], and to work under mild conditions, which can avoid polymer degradation and deformation. Moreover, many cheap technologies are available to apply these hybrid coatings to items with even a complex geometry.

When organic oligomers or polymers are incorporated in the initial solution, along with the metal alkoxides typically used in the traditional sol–gel approach to prepare all inorganic glasses, a hybrid nanostructured material with organic and inorganic domains forming distinct but strictly interconnected phases can be obtained. Functional properties can be added by including suitable additives in the initial solution.

The possible improvement of surface properties that can be obtained by applying hybrid coatings to plastic substrates can be nullified by poor intrinsic properties of the coating or poor adhesion to the substrate [9]. Thus, coating mechanical properties and adhesion to the substrate are

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major issues to be controlled, possibly by developing purposely tailored coating compositions or by specific preliminary surface treatments of the substrate.

In order to assess coating mechanical properties and adhesion, various experimental techniques have been proposed, including nanoindentation, scratch and fragmentation tests.

Nanoindentation allows to determine indentation modulus, hardness [10], residual stresses and fracture toughness of the coating and the fracture toughness of the coating-substrate interface [11,12]. The method, developed for purely elastic inorganic coatings, can be modified to take into account the viscoelastic nature of hybrid organic–inorganic coatings [13]. However, it has to be noticed that, for thin coatings, this kind of characterization can be strongly affected by modulus and hardness of the substrate.

Scratch tests can be considered a particular type of indentation and the measured critical load for detachment has been used to derive information about the coating-substrate adhesion [14]. However, again, it can hardly be applied to thin coated plastic films.

The fragmentation-test method has also been used to investigate both inorganic [15] and hybrid coatings [16], and it appears more interesting than other methods to investigate the mechanical properties of thin brittle coatings as it allows to measure, in just one test, modulus and cohesive strength of the coating, as well as its adhesive strength to the substrate.

In a previous work, hybrid coatings were applied to a rigid substrate such as PMMA [16], using polycaprolactone (PCL) oligomers as organic component. It seemed to us interesting to extend a similar study to a less rigid viscoelastic substrate, such as LDPE commercial films. However, when PCL was used as organic component, no adhesion was observed, even at visual inspection. Several other polymers were tested, and only when we used polyethylene–poly(ethylene glycol) di-block copolymers the adhesion was apparently good.

So, in this work a PE–PEG–Si/SiO₂ hybrid coating with organic/inorganic mass ratio ranging between 1:2 and 2:1 was prepared by sol–gel process and spin coated on untreated and plasma treated LDPE films. The coating properties and coating-substrate adhesion were investigated using fragmentation test and the results were discussed with respect to the organic–inorganic content and substrate plasma pre-treatment.

2. Experimental

2.1. Materials

A commercial bubble-extruded 50 µm LDPE film supplied by Polimeri Europa S.p.a., with MFI = 3.5 g/10 min and density of 0.924 g/cm³, was used as polymer substrate for hybrid coatings, either as received or after plasma treatment. High purity tetraethoxysilane (TEOS, Aldrich), 3-isocyanatopropyltriethoxysilane (ICPTES, Fluka), ethanol (EtOH, Carlo Erba), tetrahydrofuran (THF, Sigma–Aldrich), hydrochloric acid 37% solution (Sigma–Aldrich), and monohydroxy terminated polyethylene–block-poly(ethylene glycol) copolymer with $M_n \sim 2250$ 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 copolymer (PE–PEG–Si in the following) was prepared by the bulk reaction of the corresponding 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 [17].

2.3. Preparation of polymer/silica hybrids

The hybrid coatings were prepared according to the sol–gel procedure elsewhere described [17]. Briefly, the triethoxysilane-terminated copolymers (PE–PEG–Si) was dissolved along with TEOS in warm THF under magnetic stirring at the concentration of 30% w/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 before spin-coating deposition on the LDPE substrate. The final hybrids were coded as “O/I x:y”, in which x:y represents the nominal mass ratio of organic (O) and inorganic (I) components assuming the completion of the hydrolysis and condensation reactions reported in the Scheme 1 and including the SiO₂ deriving from PE–PEG–Si. The polymer/SiO₂ mass ratio, O/I, was varied from 2:1 to 1:2.

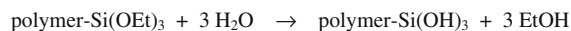
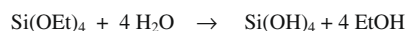
2.4. Plasma treatment of LDPE

Samples of the LDPE film were subjected to plasma treatment (in air) using a 13.56 MHz radiofrequency reactor, Plasmod 1645, supplied by March Instruments Inc. The reactor pressure was 0.1 Torr (≈13 Pa), the gas flow rate was 7.7 cm³/min, the power was set at 15 W and the treatment time was 2 min.

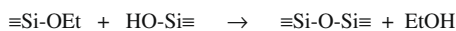
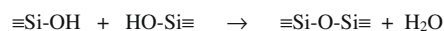
2.5. Deposition and thermal curing of hybrid coating onto LDPE films

Polymer/TEOS homogeneous solutions prepared according to the procedure previously described were

Step 1. Hydrolysis



Step 2. Condensation



Scheme 1. Hydrolysis and condensation reactions involved in the sol–gel process.

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