OXYGEN PERMEABILITY OF NOVEL ORGANIC-INORGANIC HYBRID MATERIALS COATED ON POLYETHYLENE

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Abstract

The oxygen barrier properties of composite materials, consisting of a 45 μm thick LDPE substrate coated by a thin layer (0.7-1 μm) of nanostructured hybrid organic/inorganic materials based on SiO_2 and polyethylene-polyethylene glycol (PE-PEG) block copolymers, obtained via a sol-gel technique have been characterized at 35°C and 50°C. A significant decrease (25-40%) of the oxygen transfer rate has been observed for coated samples with respect to bare substrate both at 35°C and 50°C.
The barrier effect was further improved by adding of a second organic component capable of forming hydrogen bonds, namely poly(4-hydroxy styrene) (PHS): use of PHS leads to a remarkable decrease (50 - 70 %) of the oxygen transfer rate both at 35°C and 50°C. It has been determined that the optimal formulation is the one containing 22% of PHS and 33% of silica; the thickness required for the multilayer sample to have the same barrier properties as a 45 μm thick, homogenous film composed of HDPE, oPP and PLA is equal to 2.5, 0.2 and 0.1 μm respectively.

Introduction

In the last few years a new class of materials with nanophasic morphology, the ceramers, has been proposed and developed by exploiting the sol–gel chemistry. [1-3] Ceramers are hybrid materials composed of organic and inorganic moieties, the inorganic fraction being generally based on silica. The peculiar properties of this kind of organic/inorganic hybrids result from the synergism between the properties of the polymer composing the organic phase (tenacity, flexibility, transparency, processability, low cost and good adhesion to substrates) and those of the inorganic component (toughness, flame retardancy, chemical and thermal stability, gas barrier effect). Ceramers are characterized by a stronger interaction between the organic and inorganic phase with respect to conventional nanocomposite materials, due to the covalent bonds that form between them. Many works have been carried out in order to investigate the properties of these materials: in particular, the oxygen barrier properties are crucial features for the use in food packaging industry because they affect the shelf life of the packaged food [4-6].

It is indeed the main objective of this work to focus on the oxygen barrier properties of a common polymeric material, such as LDPE, coated by a thin layer of organic-inorganic hybrid, where a copolymer PE-PEG has been chosen as organic phase and TEOS is the silica precursor. Different organic/inorganic ratios and different PE-PEG molecular weights have been investigated and the effect of the addition of a hydrogen-bonding-capable group (PHS) in the organic phase was tested [7-8].

Materials and methods

The organic inorganic hybrids were prepared following a procedure described elsewhere [7]. Briefly, most of the hybrid coatings were prepared by dissolving TEOS and triethoxysilane terminated copolymers (PE-PEG(n)-Si) in warm THF under magnetic stirring at the concentration of 30% wt./v. Water, EtOH and catalyst (HCl or NaOH) were added in the following molar ratios with respect to the overall ethoxide groups (deriving both from TEOS and functionalized copolymers): EtO-:H_2O:EtOH:catalyst = 1:1:1:0.05, and finally partially cured in a closed vial at 60°C for 2 h before deposition on the LDPE substrate by spin-coating. Table 1 summarizes the main composition data for all the hybrid coatings tested and reports data about the film thickness, as measured by SEM from the cross-sectional view of the coated films (see Figure 1 as an example).

Table 1, List of uncoated and coated LDPE films analyzed

Code	**Sample**	**Film thickness (lm)**	**M_n (PE-PEG) (g/mol)**	**Coating composition**		
				PE-PEG	**SiO_2**	**Additive (type [(d)])**
LDPE	Uncoated	45	-	-	-	-
H67	coated PE-PEG-Si/SiO_2	45 + 0.72	2250	0.33	0.67	-
H50	coated PE-PEG-Si/SiO_2	45 + 0.82	2250	0.50	0.50	-
H33	coated PE-PEG-Si/SiO_2	45 + 1.00	2250	0.67	0.33	-
L67	coated PE-PEG-Si/SiO_2	45 + 0.72	920	0.33	0.67	-
L50	coated PE-PEG-Si/SiO_2	45 + 0.82	920	0.50	0.50	-
L33	coated PE-PEG-Si/SiO_2	45 + 1.00	920	0.67	0.33	-
H00	coated PE-PEG	45 + 5.0	2250	1.00	0.00	-
H33-S22	coated PE-PEG-Si/SiO_2/PHS	45 + 1.00	2250	0.45	0.33	0.22 (PHS)
H67-S11	coated PE-PEG-Si/SiO_2/PHS	45 + 0.75	2250	0.22	0.67	0.11 (PHS)
H33-S44	coated PE-PEG-Si/SiO_2/PHS	45 + 1.00	2250	0.22	0.33	0.44 (PHS)
H00-S20	coated PE-PEG/PHS	45 + 5.0	2250	0.80	0.00	0.20 (PHS)
H00-S40	coated PE-PEG/PHS	45 + 5.0	2250	0.60	0.00	0.40 (PHS)

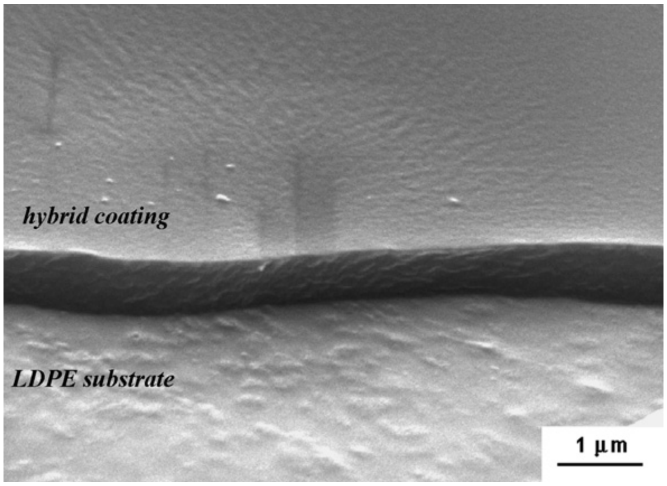

Figure 1, SEM micrograph of the edge view of LDPE film coated with H50 hybrid coating.

Pure oxygen permeability (0% R.H.) in the films was investigated by means of a closed-volume manometric apparatus, already described elsewhere [7-9] and especially designed to characterize ultra barrier films. The value of the Oxygen Transfer Rate, *O.T.R.*, which is defined in terms of the steady state gas flux, J_{SS}, and the pressure difference, Δp, is then calculated from the experimental data as:

$$O.T.R. \overset{DEF}{\equiv} \frac{J_{SS}}{\Delta p} = \left(\frac{dp_d}{dt}\right)_{t\to\infty} \cdot \frac{V}{R \cdot T \cdot A} \cdot \frac{1}{\Delta p} \qquad (1)$$

where A is the area of the sample, V is the downstream volume, R is the universal gas constant, and p_d is the downstream pressure. The *O.T.R.* value in this work is expressed in cm^3(STP)/(cm^2 d atm). The characteristic time of the diffusion process can be evaluated using the time lag value (θ_L), that is the intercept on the t axis of the pd vs. t curve after steady state, represented by a constant value of the slope, has been reached (as shown in Figure 2). If p_d is negligible compared to the upstream pressure, as it is the case of our experiments, and the film is initially gas-free, the time lag value (θ_L) is related to the diffusivity, D, of the gas in the material, through the following equation [10]:

$$\vartheta_L = \frac{l^2}{6 \cdot D} \qquad (2)$$

where l is the sample thickness.

The permeability of each layer, P_i, can be evaluated combining the *O.T.R.* of the multilayer sample with the one of the substrate through the series-resistance formula:

$$\frac{1}{O.T.R.} = \sum_i \frac{1}{(O.T.R.)_i} = \sum_i \frac{l_i}{P_i} \qquad (3)$$

where l_i is the thickness of each layer i. The permeability, which is a material property not depending on the geometry of the sample, was used to compare the transport properties of different coatings. In this work, the permeability is numerically expressed in Barrer (1 Barrer = 10^{10} [(cm3(STP)cm)/(cm^2 s cmHg)]).

Results and discussion

Experimental values of the oxygen transport properties (*O.T.R.* and the related time-lag) of the various samples measured at 35 and 50°C are listed in Table 2.

Table 2. Oxygen transfer rate and time-lag values in the various samples at 35°C and 50°C.

	35°C		**50°C**	
Code	**O.T.R.** $cm^3(STP)/(cm^2 \cdot d \cdot atm)$	**time-lag** s	**O.T.R.** $cm^3(STP)/(cm^2 \cdot d \cdot atm)$	**time-lag** s
LDPE	0.675	4.7	1.413	1.9
H67	0.390	7.3	0.916	3.3
H50	0.436	7.0	1.001	3.1
H33	0.410	7.1	1.064	2.9
L67	0.523	6.5	1.135	2.8
L50	0.538	6.7	1.201	2.9
L33	0.501	6.8	1.122	3.0
H00	0.316	6.2	0.826	1.3
H33-S22	0.194	6.2	0.615	2.6
H67-S11	0.358	6.0	0.737	4.2
H33-S44	0.296	9.4	0.572	1.4
H00-S20	0.253	5.3	0.843	1.0
H00-S40	0.291	10.3	0.836	2.5

(Maximum uncertainty: ±2.5 % for *O.T.R.*; ±7.5 % for time lag values)

Although the overall thickness of the hybrid coating is typically lower than 1 μm, in most cases the permeance of LDPE is remarkably reduced after addition of the coating, and the improvement is comparable with the one observed in case of plastic filled with Montmorillonite [11-12]. The results in terms of time-lag values show that the hybrid coating also allows to slow down remarkably the permeation process, due to a slower kinetics of diffusion.

While there is only a limited effect of the organic–inorganic ratio on both *O.T.R.* and time-lag, significant increase of *O.T.R.* (10–20%) and a slight decrease of time-lag (about 5%) are due to the decrease of the molecular weight of the PE-PEG organic component from 2250 to 920 g/mol; the higher free volume in organic domains associated with the lower molecular weight may be responsible of this behavior.

In order to have a more meaningful comparison between the properties of the different hybrids, the permeabilities of the pure coatings have been evaluated according to Eq. (3). The calculated values at 35 and 50°C are reported in Barrer and listed in Table 3.

Table 3, Oxygen permeability in LDPE and pure coatings at 35 and 50°C

Code	**Permeability (Barrer)**	
	35°C	**50°C**
LDPE	4.625	9.683
H67	0.101	0.285
H50	0.154	0.428
H33	0.159	0.657
L67	0.247	0.615
L50	0.332	1.003
L33	0.296	0.831
H00	0.451	1.512
H33-S22	0.041	0.166
H67-S11	0.087	0.176
H33-S44	0.080	0.146
H00-S20	0.307	1.590
H00-S40	0.389	1.561

The so-obtained results were analyzed on the basis of the Maxwell model which predicts a permeability reduction as follows [13]:

$$\frac{P}{P_0} = \frac{1-\phi}{1+\phi/2} \tag{4}$$

where P_0 is the permeability in the pure material and ϕ is the volumetric fraction of the inorganic phase, (estimated by assuming the density of the organic and inorganic phases equal to 1 and 2 g/cm^3, respectively). The data calculated from eq. 4 for the case of PE-PEG/Si-SiO$_2$ hybrids are plotted as dotted lines in Figure 2, together with the experimental data.

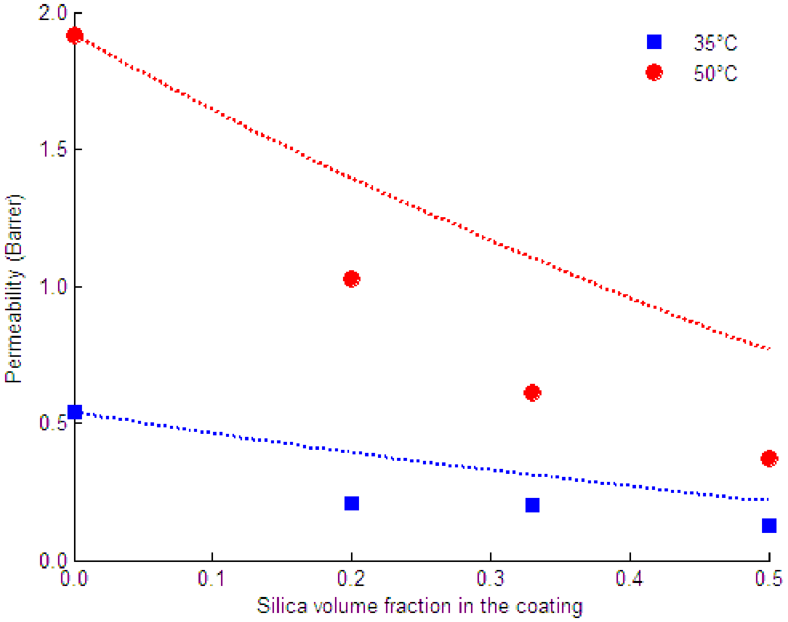

Figure 2, Oxygen permeability of coatings containing PE-PEG with M_n = 2250 g/mol at 35 and 50°C. Experimental results (squares, 35°C, and circles, 50°C) are reported along with the curves (dotted lines) calculated from the Maxwell model

As one can see, the experimental points, both at 35°C or 50°C, lie below the curves calculated by the Maxwell equation. These results suggest that, for the organic-inorganic hybrid material prepared under acidic conditions, the improvement of the barrier properties is more significant then predicted by Eq. 4 for conventional composite materials in which the two phases do not interact, due to a synergetic effect existing between the two phases.

On the other hand, all coatings containing PHS showed permeabilities quite lower then that in the PE-PEG-Si/SiO_2 hybrids, both at 35°C and at 50°C and stronger barrier effects were obtained for the coating with intermediate amount of silica and PHS (H33-S22). However, the effect of the addition of PHS on permeability is not monotonous with PHS content, but there exists a minimum, that has to be located at around 20 wt. % of PHS. The existence of a minimum is not surprising and may be due to different issues that occur at high concentrations of PHS such as the saturation of the hydrogen bonds that silanol groups can form with PHS, and, to a lower extent, with ether groups of PE-PEG or poor miscibility between the two organic components, that can induce phase separation of PHS, limiting the formation of hydrogen bonds with silanols.

To describe the permeation behavior of the polymer blend we used a simple mixing rule that neglects the mutual interactions between the two polymers:

$$P_{org} = x_{PHS} P_{PHS} + x_{PE-PEG} P_{PE-PEG} \qquad (5)$$

where x_{PHS} and $x_{PE\text{-}PEG}$ are the molar fractions (calculated considering the average molecular weights of the organic species) of the two components in the organic phase and P_{PHS} and $P_{PE\text{-}PEG}$ are the pure polymers permeabilities; once the theoretical permeability of the organic phase is calculated, Eq. 4 can be then applied to predict the barrier properties for a heterogeneous material.

In Figure 3, the data estimated by Eqs. (4) and (5) are reported as continuous lines and are compared to the experimental ones and to the value of pure PHS permeability taken from the literature at 35°C [14].

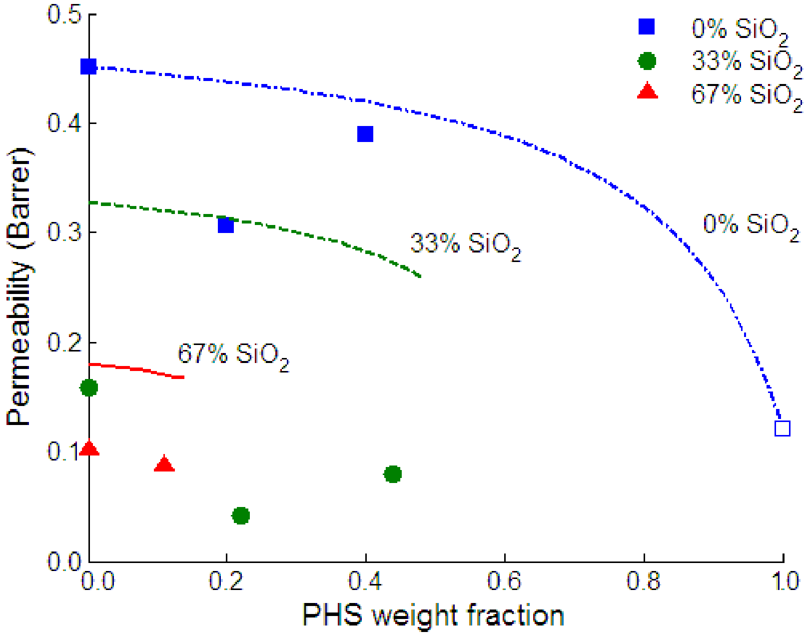

Figure 3, Permeability in organic/inorganic hybrid at 35°C, curves are due to the model in Eqs. (4,5). The open symbol is taken from the literature [14]

Considering at first just the polymer blend by itself, and comparing the experimental data with those calculated by the additive rule expressed by Eq. (4), we notice that at low PHS content the experimental permeability of the system is lower than that predicted by the additive rule, meaning that a synergic effect takes place between the two polymers, that may be due to the formation of hydrogen bonds between PHS and PE-PEG segments. For higher PHS content, the system seems to follow more closely the additive behavior represented by Eq. (4).

When considering the ternary system, containing also the inorganic component, it can be seen that the hybrid permeability is, as previously observed for the case with no PHS, much lower than that calculated on the basis of Eq. (4), representative of the permeability of a filled system obtained by physically dispersing the same volume fraction of spherical silica. This result can indeed be attributed to the fact that the coating molecular architecture consists of a highly interpenetrated network of organic and inorganic phases rather than of a physical dispersion of spherical silica particles in the organic phase.

Conclusions

It has been shown how a thin layer of organic-inorganic hybrid coating can be used to improve oxygen barrier properties of plastic films. The use of a suitable polymer (PE-PEG) within the coating allows to obtain good adhesion to the LDPE substrate without any previous surface treatment. The oxygen permeability decreases with increasing molecular weight of the organic phase and with increasing silica weight content. Furthermore, the inclusion of a second polymeric phase, PHS, able to form hydrogen bonds has been explored and it has been shown that it allows to increase further the barrier effect. The experimental results have been compared with those calculated by using simple models describing the permeability of polymer blends and conventionally filled particulate composites, allowing to evidence significant contributions of morphology and hydrogen bonds to the reduction of the permeability.

The easy processability of these coatings suggests that they are a convenient alternative approach to the improvement of oxygen barrier properties with respect to the conventional composites obtained by clay dispersion in polymeric matrices.

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