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Perhydropolysilazane derived silica for flexible transparent barrier foils using a reel-to-reel wet coating technique: Single- and multilayer structures

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ABSTRACT

The paper concerns investigations of the coating and the converting conditions of perhydropolysilazane (PHPS) for the creation of SiO_x including multilayer setups for application in transparent gas barrier foils. The use of different substrates and several organic intercalated layers was proofed also in reel-to-reel (R2R) coating processes. A lowering of the gas permeation against oxygen and water could be found for the coated foils under maintaining the optical transparency of the pristine foils. With one SiO_x layer (600 nm) coated by R2R and converted at low temperature a reduction of the oxygen transmission rate (OTR) from 11 $cm^3/(m^2$ d bar) of pure 125 μm polyethylene terephthalate (PET) to 0.09 $cm^3/(m^2$ d bar) of PET/SiO_x could be observed. Taking advantage of the so-called “tortuous path effect”, we obtained OTR values below 0.05 $cm^3/(m^2$ d bar) (detection limit of the Mocon test) with 3- or 5-layer-systems. The films are highly optically transparent and can exceed the light transmission of the uncoated substrate using an optimized layer stack with respect to thickness and refractive index.

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1. Introduction

Protection of organic electronic devices like organic light emitting diodes (OLEDs) or organic photovoltaic (OPV) cells against oxygen or water is necessary to minimize degradation [1,2]. This is a great challenge for flexible devices. Water vapor transmission rates (WVTR) and oxygen transmission rates (OTR) of transparent high barrier foils are required to reach about 10^{-6} $g/m^2/d$ and 10^{-3}–10^{-5} $cm^3/m^2/d/bar$, respectively [3].

Moreover, materials and processing costs of these foils should minimally add to the overall device costs. This calls for production technologies of barrier layers enabling cost-effective large area reel-to-reel (R2R) coating from solutions.

Polymer materials are always more or less permeable for gases because of the nature of the polymer chains, their disorder and the low density in bulk. The polarity and the structure (the degree of crystallization, density) are most important factors, which influence the gas transport but cannot fully prevent it. Commonly used pure polymeric materials, e.g. for plastic food packaging, have OTR and WVTR values in the range of 10^2–10^1; only a few special ones gain up to 10^0 (with thicknesses of 100 μm) [4].

One option for reaching higher permeation-barriers is the increase of the thickness of the polymer film. As a consequence the foils become more rigid and a lesser flexibility hinders an application. The blending of polymers with inorganic particles (high aspect ratio) represents another option to extend the path length for penetrating molecules [5], but this normally corresponds with changes of other material properties. Also the co-extrusion of polymers to combine good WVTR with good OTR properties cannot reach barrier levels below 10^{-2}. Inorganic materials (aluminum for instance) accomplish the best barrier performance. Those can even be applied as a very thin layer but with the loss of optical transparency as a disadvantage [6,7]. Suitable candidates for transparent layers are for instance AlO_x, Al_2O_3, SiO_x, TiO_x, SiN_x, Si_3N_4, SiON, and ZnO, whose application requires vacuum processes (physical vapor deposition (PVD)/chemical vapor deposition (CVD)/atomic layer deposition (ALD)) in general [8]. At least, ultra high barriers with the aimed values for the protection of plastic electronics can be obtained by using those inorganic layers in an alternating inorganic–organic multilayer setup [9–11]. The defects in an inorganic layer, which are responsible for the gas permeation leftover, are filled by an organic coating. If an inorganic layer is repeatedly covered in an alternating mode, the pinholes become decoupled as well. But, a high pricing machinery, the energy consumption and long processing times (ALD) prevent low cost barrier foils coming to market currently. Proceeding from this the motivation derives for the here presented work. Liquid processing by using wet coating instead of vacuum technologies is a promising route to lower production costs. The materials establishing the inorganic barrier (e.g. metal oxides) can be prepared in ton-scale and be applied from suspensions in very thin, material saving layers (10 nm–10 μm) by a

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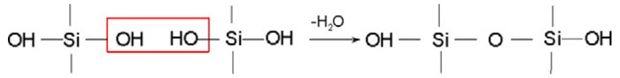
reel-to-reel slot-die-coating process to combine a fine adjustment of layer thickness with a high through-put potential [12].

One material of growing interest in this manner is perhydropolysilazane (PHPS) [13]. In the presented article it is the base material and can fulfill the requirements to receive high-barriers for instance for OPV encapsulation [14] or even for covering CIGS-modules because of its optical properties [15]. After the wet coating and the evaporation of the solvent PHPS can be transformed into a SiO_x-material. For this purpose a hydrolysis of the Si—N—bonds with the elimination of hydrogen and ammonia is proceeded

$$—(SiH_2NH)— \; + \; 2\,H_2O \; \rightarrow \; —(Si(OH)_2)— \; + \; H_2 \; + \; NH_3$$



The conversion to an inorganic barrier material can be done thermally or photochemically [17] and can be influenced by several parameters (e.g. water/ammonia vapor, catalysts, ozone, UV) [18–21]. A rapid thermal conversion at temperatures above 200 °C is not applicable to most polymer substrates. But a low temperature curing (below 100 °C) is also possible, while the curing times prolong to days or weeks. An alternative route is the conversion by UV [22,23], especially at short wave lengths (vacuum–UV VUV, $\lambda = 172$ nm). The current focus in the research to PHPS lies on VUV as well as on low-temperature conversion [24,25] and on R2R-processing (from single-layers to laminates) respectively, as Prager et al. report [26,27].

Data from literature show the potential for a PHPS derived silica application: Single-layers (250 nm SiO_x from PHPS on 50 μm PET; bar-coating; VUV curing) are described by Morlier et al. [14] with 0.06 $cm^3/m^2/d/bar$ OTR and 0.2 $g/m^2/d$ WVTR, in multilayer-stack with two SiO_x-layers and polyvinyl alcohol as an intercalated layer $<10^{-3}$ $cm^3/m^2/d/bar$ OTR and 0.02 $g/m^2/d$ WVTR. In [26] Prager and Buchmeiser et al. demonstrate R2R-coating by using PHPS and give values for OTR 1 $cm^3/m^2/d/bar$ and WVTR <4 $g/m^2/d$ of R2R-coated samples (36 μm PET, <100 nm SiO_x; VUV curing) for a single layer from a mixture of PHPS and a methyl-substituted derivative of it. To our knowledge R2R produced multilayer-stacks are not described in the literature presently. Even more input on material variety is necessary (films and organic layers).

Our approach starts with these considerations, with the intention to investigate the variations in coating and converting conditions for a SiO_x containing multilayer setup. In Fig. **1** the architecture and the scope of our work relating to different substrates (foils) and organic interlayers are presented. The technological scale covers spincoating up to large-area R2R-wet-coating and goes from single- to multi-layer structures. The R2R-coating system equipped with an excimer lamp ($P = 60$ W corr. to 80 mJ/cm^2 @ 1 m/min) converts the silica based raw material via VUV in-line, so as to compare with thermally converted layers. The aim was not the clarification or optimization of the conversion or the reaction mechanism, respectively. The primary task was the realization of a well-functioning layer-setup or formation of layers as well as the variation of the coating parameters (wetting, layer thicknesses, defects) to study their influences on the barrier properties against oxygen and water vapor. The purpose of the work is to take the next step towards a prospective barrier-foil production by making a contribution to R2R-coated multilayer-stacks and material diversity.

2. Experimental

2.1. Materials

Employed materials for transparent plastic films were PET-foils Hostaphan RN 125 PET (biaxially oriented polyethylene terephthalate, colorless transparent, 125 μm, 300 m, 20 cm), unspecified PET (colorless transparent, 71 μm, 300 m, 14 cm) and PP-foil (OPP TSS 48 T, biaxially oriented polypropylene film, sealing layer on both sides with one side pretreated for printing, 48 μm, 300 m, 20 cm) purchased from Pütz GmbH + Co. Folien KG. A 100 μm polypropylene foil (20 cm) was manufactured from PP H105-03NA (DOW) at a Göttfert extrusiometer (200–250 °C). The Colamin2 foil (60 μm polyethylene (PE)/10 μm ethylene vinylene alcohol–copolymer (EVOH)/50 μm polyethylene (PE), 120 μm, 200 m) was obtained from Obermühle Polymertechnik GmbH and the Moldflon® base foil from Fa. Elring Klinger Kunststofftechnik GmbH (fluoropolymer foil, 100 μm, pretreated from supplier with PVD-layer). The perhydropolysilazane (PHPS) NL-120-05A (contains a catalyst, 5 wt.% PHPS in di-*n*-butyl ether $\rho = 0.79$ g/cm^3, Clariant) and NN-120-20 (contains no catalyst system, 20 wt.% PHPS in di-*n*-butyl ether, AZ Electronic Materials Germany GmbH) were purchased and not filtered prior to use. PVdC (polyvinylidene chloride) solution (15 wt.% in tetrahydrofuran/toluene 2/1) was prepared by stirring PVdC from Asahi Kasai for 2 h at 50 °C and filtered prior to use (2.7 μm). The 10 wt.% solution of EVOH (ethylene vinylene alcohol–copolymer) was freshly prepared before coating by stirring an EVOH granulate — EVAL F101A (from EVAL Europe) — in dimethyl formamide (DMF) at 160 °C for 1 h. The solution was not filtered prior to use and was kept at 100 °C and applied warm in a spincoating procedure (rotation speed: 400 rpm for 3 min). Another EVOH formulation: commercial Aquaseal X2281 (20 wt.%, ethylene vinylene alcohol–copolymer in H_2O, 500 mPas (23 °C), pH 5.5, applied in spincoating with a rotation speed of 600 rpm for 3 min or applied in reel-to-reel-coating with a velocity of 1 m/min with a given volume flow) and a polyolefin dispersion Aquaseal X2200 (20 wt.% ethylene/octene–copolymer in H_2O, filtered prior to use 2.7 μm filter, 150 mPas (23 °C), pH 11, applied in spincoating with a rotation speed of 400 rpm for 3 min) were obtained from *paramelt*. Silicon wafers (380 μm, single side polished, Si-Mat Silicon Materials) were used for IR-measurements.

2.2. Methods

Surface energies were determined with a contact angle/surface tension measuring instrument DSA100 by Krüss. The thickness of the coated layers was determined by a Woollam spectral ellipsometer M44

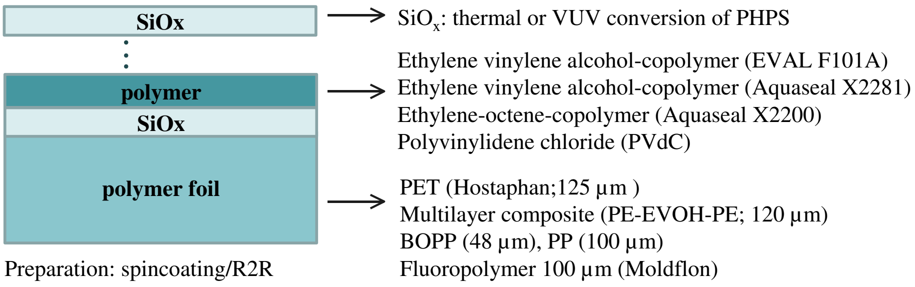


Fig. 1. Layer stack of wet-coated barrier foils and used materials.

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