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Roll-to-roll thin film coating on fluoropolymer webs – Status, challenges and applications

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ABSTRACT

Thin film deposition on fluoropolymer webs – both in vacuum and at atmospheric pressure – faces several critical challenges such as poor mechanical and thermo-mechanical properties – especially low dimensional stability and low elastic modulus, high and textured surface roughness and low adhesion of thin films.
This paper discusses critical process parameters in roll-to-roll processing for both vacuum processes and wet coating processes with respect to the unique properties of fluoropolymer webs. Reactively sputtered oxide layers as well as wet coated ORMOCER® layers are deposited on ETFE, PVDF and ECTFE webs to form single- and multi-layer permeation barrier systems. The influence of relevant process parameters on the layer adhesion and permeation barrier performance is reviewed. Permeation barrier coatings have been selected as main application for this study, because they are very sensitive to substrate surface irregularities and mechanical damage due to low adhesion, high strain or roll-to-roll processing issues and therefore are a good measure for the quality of the coating on the substrate.
Both the wet coated ORMOCER® layers and reactively sputtered zinc-tin oxide (ZTO) layers show surprisingly good adhesion on both ETFE and PVDF surfaces. Both ZTO and – with adhesion promotion treatment – also aluminum oxide (Al_2O_3) layers have the potential for low water transmission rates (WVTR) below $5 \cdot 10^{-2}$ g/(m^2 d) at 38 °C/90% r.h. on these substrates. Further reduction of the WVTR is demonstrated with a combination of wet coated ORMOCER® layers and sputtered ZTO layers yielding a WVTR of $1 \cdot 10^{-3}$ g/(m^2 d) at 38 °C/90% r.h. These values were achieved using adapted process parameters and layer stack designs such as reduced web tension and lower layer thicknesses. The results shown in this paper demonstrate the potential of coated fluoropolymer webs for functionalization of membrane roofs and façades with flexible thin film solar cells; thermal insulation and solar control functionality; flexible thin film electroluminescent and OLED lighting panels as well as electrochromic devices.

1. Introduction

Fluoropolymers are widely used in a variety of applications because of their outdoor and weathering and their high optical transparency [1]. A large area application for webs and fabrics made of fluoropolymers is the membrane architecture esp. membrane roof or façade elements [2]. Typical materials used are e.g. ethylene tetrafluoroethylene (ETFE), polytetrafluoroethylene (PTFE) or polyvinylidene fluoride (PVDF). They are integrated into membrane cushions either as bare polymer web or coated with a printed colored layer. Only few publications are available addressing vacuum coating or plasma processing on those substrates [3–8]. Most research on thin film coatings on polymers is done on PEN or PET films as these materials are widely available with – depending on the specific commercial product used – superior surface quality and smoothness, with favorable mechanical properties (esp. elastic modulus in machine direction) and with reasonable temperature stability for typical processing temperatures up to 150 °C [9]. A few authors reported on concepts for low-emissivity heat protection coatings on ETFE by using sputtering methods [1,6,7]. Siefert et al. demonstrated successful roll-to-roll deposition of an oxide – metal – oxide infrared light reflection stack on ETFE that survived 30 days in a climate chamber at 80 °C and 80% relative humidity (r.h.) [7]. Atomic layer deposition of Al_2O_3 and TiO_2 on ETFE and PETFE surfaces has been discussed by Kemell et al. for the purpose of altering the water contact angle and surface energy of these fluoropolymer webs in a batch process at elevated substrate temperatures [8]. The authors experienced low adhesion of both Al_2O_3 and TiO_2 on both substrates. Crack formation was observed

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for any Al_2O_3 coatings on both ETFE and PTFE. The authors stated sample handling as possible reason for crack formation. However, they did not discuss potential influence of thermal expansion or other temperature related issues due to the deposition temperature which was varied between 80 °C and 250 °C and did their experiments in a batch process.

The integration of thin film solar cells into ETFE membrane elements has been evaluated in a study by Cremers et al. – using devices that were deposited on polyethylene terephthalate (PET) webs and subsequently laminated onto the outer layer of an ETFE membrane cushion [1]. The authors mentioned thermally induced stress and cracking due to long term flow behavior of the substrate as potential issues for coatings directly on ETFE.

A recent own publication discussed first results on the preparation of permeation barrier layers and layer stacks on ETFE using reactively sputtered zinc tin oxide (ZTO – Zn_2SnO_4) layers and wet coated ORMOCER® interlayers [10]. Water vapor transmission rates below $5 \cdot 10^{-2}$ g/(m^2 d) (at 38 °C/90% r.h.) have been reported for both single and multi-layers. The elastic properties of the ETFE films were identified as critical for both vacuum and wet coating. Mechanical stress resulted in high water vapor permeability of both single and multi-layer barriers.

Based on the results of our earlier work, this paper discusses improved process parameters for vacuum roll-to-roll plasma surface treatment and coating of fluoropolymer webs, in particular ETFE and PVDF films, with respect to the specific thermomechanical and surface properties of the substrate material. Layer adhesion promotion techniques will be evaluated by using different types of pretreatment of the ETFE surface. Finally, single and multilayer permeation barriers have been applied on ETFE webs using optimized process parameters compared to our earlier publication and have been compared to systems that were deposited on PET and PEN substrates. The permeation barrier performance has been chosen as measure for the coating quality as barrier layers are very sensitive to coating failures. Causes for such failures are e.g. low layer adhesion, surface irregularities on the substrate and mechanical damage due to shrinkage, strain or roll-to-roll processing issues [11]. Except mentioned own work no results were reported on thin film permeation barrier coatings on ETFE or other fluoropolymers yet.

2. Experimental procedures

2.1. Polymer substrates

The following polymer substrates have been used as substrate and reference materials for this study: ETFE: ET6235-Z with a thickness of 100 μm provided by NOWOFOL Kunststoffprodukte GmbH & Co. KG, Germany; PVDF nowoflon PVDF with 80 μm thickness and ethylene chlorotrifluoroethylene (ECTFE) with 50 μm thickness, both also from NOWOFOL Kunststoffprodukte GmbH & Co; PTFE with 30 μm thick (MOLDFLON® from ElringKlinger Kunststofftechnik GmbH, Germany) and finally PET Melinex® 401 CW (75 μm), Melinex ST504 (125 μm) and Polyethylene-naphthalate (PEN) Optfine PQA 1 (125 μm), all from DuPont Teijin Films. PET and PEN were used as reference materials for comparing the coating performance on the fluoropolymer webs with well-known substrates. The selection of fluoropolymer materials was made with respect to the desired applications such as membrane roof and façade elements as well as solar front sheets, where e.g. ETFE is already in use either in a laminate or as uncoated front sheet film [12,13].

2.2. Coating equipment and processes

All vacuum coating experiments have been performed in a continuous roll-to-roll process on a coating width of 400 mm. The vacuum roll-coater *coFlex® 600* with a maximum coating width of 650 mm has been used to deposit zinc-tin-oxide (Zn_2SnO_4, ZTO) and aluminum oxide (Al_2O_3) layers and to perform the plasma-surface treatment experiments. With respect to the targeted application as front-side encapsulation film for flexible solar cells, focus was lying on low water vapor transmission rates of the coated web. ZTO and Al_2O_3 were found to have lowest WVTR among reactively sputtered barrier materials and were therefore used for this study [14]. The machine, shown in an earlier publication [15], contains six dual magnetron systems that are arranged around two cooled process drums. The target size of each dual magnetron was $2 \times 900 \times 183$ mm^2. A controlled reactive sputtering process has been used with metal alloy targets (52 wt.% zinc and 48 wt.% tin) for ZTO and Al metal targets for Al_2O_3 deposition. The reactive gas flow (oxygen) has been controlled using the optical emission of excited metal atoms in the plasma as control variable in a proportional-integral-differential control loop. ZTO barrier layers have been deposited directly on the substrates without any further pretreatment. The process drum was cooled to 10 °C in all experiments. Web speed was adjusted between 0.2 m/min to 2.5 m/min to deposit layer thickness between 25 nm and 150 nm.

The ORMOCER® coating was applied in the 400 mm wide roll-to-roll wet coating machine described in [15] using a reverse gravure coating process with subsequent thermal curing at 120 °C. Web-tension was $1.5 \cdot 10^6$ N/m^2 for the fluoropolymer substrates and $2.5 \cdot 10^6$ N/m^2 for the PET substrate. The fluoropolymer surface was corona-pretreated before ORMOCER® deposition. The term ORMOCER® (registered trademark of the Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V., Munich) refers to a special material class of inorganic-organic hybrid polymers, containing an inorganic *Si*-O-Si backbone with organic crosslinking and organic moieties. The properties of ORMOCER® resins and lacquers can be specially adapted by the experienced variation of composition and synthetic parameters with respect to different applications and use cases [16].

2.3. Methods for layer characterization

Water vapor permeability was measured using a carrier gas based measurement device with a coulometric sensor from BRUGGER Feinmechanik GmbH, Germany according to the international standard ISO 15106-3. The device has a lower limit of detection of $1 \cdot 10^{-3}$ g/(m^2 d) with a measurement uncertainty of ±2% or at least $\pm 1 \cdot 10^{-3}$ g/(m^2 d). The sample area was 78 cm^2 and the measurement conditions were set to 38 °C/90% relative humidity (r.h.) for all results presented in this study.

Cross-section images were obtained by cutting the samples with focused ion beam cross-section polisher (Jeol SM-09010) and a scanning electron microscope (SEM) HITACHI SU8000 with 1 kV electron acceleration voltage. SEM surface images were obtained using the abovementioned HITACHI SU8000 SEM with 2 kV acceleration voltage. Surface roughness was evaluated using an atomic force microscope (AFM) (TOPOMETRIX Explorer) in non-contact mode on an area of 2.3×2.3 μm^2 and – for larger scan areas – either an AMBIOS XP-200 surface profilometer averaging 10 line scans with a length of 0.5 mm or a white light interferometer (GBS SmartWLI Extended) on an area of 1×0.75 mm^2.

Optical transmittance, reflectance and absorption were measured using an UV/VIS/NIR spectral photometer Lambda 900 (PerkinElmer) in the wavelength range between 250 nm and 1300 nm with a 2 nm wavelength step. The device was set up with an integration sphere to determine the total transmittance (T) and total reflectance (R). Absorption (A) was calculated according to $A = 1 - T - R$ for each wavelength.

Adhesion has been tested using a 90° peel-test according to IPC-TM-650 standard with a TESA 7475 adhesive tape. The sample was laminated onto a carrier web that was required to mount the sample to the "Sebastian Five" peel test unit. Hence, the resulting peel force represents the adhesion force of the weakest interface in the system – which not only may be an interface in the sample but also between the lamination adhesive and the sample. Elastic moduli of the polymer films (see section 3 above) were measured at room temperature

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