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Roll-to-Roll Thin Film Coating on Fluoropolymer Webs – Status, Challenges and Applications

John Fahlteich[1], Cindy Steiner[1], Nicolas Schiller[1], Oliver Miesbauer[2]
Klaus Noller[2], Karl-Joachim Deichmann[3], Mark Mirza[3], Sabine Amberg-Schwab[3]
[1]*Fraunhofer Institute for Organic Electronics, Electron-Beam and Plasma Technology FEP, Dresden, Germany*
[2]*Fraunhofer Institute for Process Engineering and Packaging IVV, Freising, Germany*
[3]*Fraunhofer Institute for Silicate Research ISC, Würzburg, Germany*

ABSTRACT

Fluoropolymer webs and membranes commonly exhibit superior optical properties such as high transmittance over a broad wavelength range and very good outdoor stability. Therefore, fluoropolymer films are used in architecture, for example, in membrane roofs and facades in stadiums, shopping malls, and airports or as front-side encapsulation for solar cells. However, thin film deposition on fluoropolymer webs – both in vacuum and at atmospheric pressure – face several critical challenges including 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® (a trademark of the Fraunhofer Institute) layers were deposited on ethylene tetrafluoroethylene (ETFE), polyvinylidene difluoride (PVDF), and ethylene chlorotrifluoroethylene (ECTFE) webs form single- and multilayer permeation barrier systems. Layer adhesion and permeation barrier performance was reviewed in relation to the relevant process parameters. Permeation barrier coatings were selected as lead application for this study. Barrier coatings are sensitive to substrate surface irregularities and mechanical damage due to low adhesion, high strain, or roll-to-roll processing issues and therefore were a good measure for the quality of the coating on the substrate.

Reactively sputtered zinc-tin oxide (ZTO) layers as well as wet coated ORMOCER® layers showed surprisingly good adhesion on both ETFE and PVDF surfaces. Both ZTO and – with adhesion promotion treatment – aluminum oxide (Al_2O_3) layers have the potential for low water transmission rates (WVTR) below 5×10^{-2} g/(m²d) at 38°C/90 % RH. on these substrates. Further reduction of the WVTR using multilayer stacks was demonstrated with a combination of wet coated ORMOCER layers and sputtered ZTO layers yielding a WVTR of 1×10^{-3} g/(m²d) at 38°C/90 % RH. To achieve that, adapted process parameters and layer stack designs such as reduced web tension and lower layer thicknesses were needed.

The potential of the coatings for specific outdoor application is discussed as well as possible ways to improve the polymer web itself to gain a larger process window for roll-to-roll coating on fluoropolymer webs. Demonstrating successful coating on ETFE and PVDF, the results reviewed in this paper potentially enable the use of coated fluoropolymer webs for functionalization of membrane roofs and facades with flexible thin film solar cells, thermal insulation and solar control functionality, flexible thin film electroluminescence, and organic light-emitting diode (OLED) lighting panels as well as electrochromic devices.

A version of this paper may be found in a special issue of Elsevier's journal, *Surface and Coatings Technology*, which includes selected work presented at the 2016 Society of Vacuum Coaters Technical Conference in Indianapolis, Indiana.

INTRODUCTION

Fluoropolymers are widely used in a variety of applications because of their outdoor and weathering stability as well as high optical transmittance [1]. A large-area application for fluoropolymer webs is in architecture, especially for membrane roofs and façade elements [2]. Typical substrate materials are ethylene tetrafluoroethylene (ETFE), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF). They are integrated into membrane cushions either as a draw bar–coated polymer web or coated with a printed coloring layer. Few studies are available on vacuum coating or plasma processing on these substrates [3–8]. Most polymers and thin film coating research has been on polyethylene naphthalate (PEN) or polyethylene terephthalate (PET) films because these materials are widely available and have superior surface quality and smoothness, favorable mechanical properties (especially good Young's modulus in the rolling direction), and reasonable temperature stability for typical processing temperatures up to 150°C [9]. Previous experiments reported on sputtering techniques for low-emissivity heat protection coatings on ETFE [1, 6, 7]. Siefert et al. [7] demonstrated successful roll-to-roll deposition of a metal oxide infrared light reflection stack on ETFE that survived 30 days in a climate chamber at 80°C and 80 % relative humidity (RH). Atomic layer deposition of Al_2O_3 and TiO_2 on ETFE and PTFE surfaces was discussed by Kemell et al. for the purpose of altering the water contact angle and surface energy of fluoropolymer webs in a batch process at elevated substrate temperatures [8]. Kemell et al. found low adhesion of both Al_2O_3 and TiO_2 on the PTFE and the ETFE substrates. Crack formation was also observed for the Al_2O_3 coatings on both ETFE and PTFE. Kemell et al. concluded that sample handling was the possible cause for cracking. Their experiment, however, did not discuss potential influence of thermal expansion or other temperature-related issues due to the deposition temperature, which varied between 80°C and 250°C. Furthermore, the coating was made in a batch sheet process and not in a roll-to-roll configuration.

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

A recent publication by our group discussed results of 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 (a registered trademark of the Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V., Munich) interlayers [10]. Water vapor transmission rates below 5×10^{-2} g/(m²d) (at 38°C/90 % RH) were reported for both single and multilayers. The elastic properties of the ETFE films were identified as critically important for both vacuum and wet coating processes, which limits the achievable water vapor transmission rate (WVTR). The possibilities for improving coating quality to lower the WVTR were not discussed. Based on the results of this earlier work, this paper discusses 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. Potential for layer adhesion promotion was evaluated by using different types of pretreatment of the ETFE surface. Finally, single and multilayer permeation barriers were applied on ETFE webs using optimized process parameters compared to earlier work [10] and were compared to systems that were deposited on PET and PEN substrates. Permeation barrier performance of the layers was chosen as a measure for the coating quality because barriers are very sensitive to coating failures caused by low layer adhesion, surface irregularities on the substrate, and mechanical damage due to shrinkage, strain or roll-to-roll processing issues [11]. No results have been reported on thin film permeation barrier coatings on ETFE or other fluoropolymers.

EXPERIMENTAL PROCEDURES

Polymer Substrates

The following polymer substrates were 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 to compare 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 for example, ETFE is in use either in a laminate or as uncoated front sheet film [12, 13].

Coating Equipment and Processes

All vacuum coating experiments were done 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, was used to deposit zinc-tin-oxide (Zn_2SnO_4, ZTO) and aluminum oxide (Al_2O_3) layers and to perform any plasma-surface treatment experiments. With respect to the targeted application as a front-side encapsulation film for flexible solar cells, the focus was on low water vapor transmission rates of the coated web. ZTO was found to have the lowest moisture vapor transmission rate (WVTR) among reactively sputtered barrier materials and was therefore used for this study [14]. The machine, shown in an earlier study [15], contained six dual magnetron systems that were arranged around two cooled process drums. The target size of each dual magnetron was 2 × 900 × 183 mm². A controlled reactive sputtering process was 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) was 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 were deposited directly on the substrates without any further pretreatment. The process drum and the backside of the polymer web was cooled to 10°C in all experiments. The web speed was adjusted between 0.2 m/min and 2.5 m/min to deposit layer thickness between 25 nm and 150 nm.

The ORMOCER coating was coated on 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/m² for the fluoropolymer substrates and $2.5 \cdot 10^6$ N/m² for the PET substrate. The fluoropolymer surface was corona-pretreated before ORMOCER deposition. The name ORMOCER refers to a special material class of inorganic-organic hybrid polymers, containing an inorganic Si-O-Si backbone and organic moieties. The properties of ORMOCER resins and lacquers can be specifically adapted by the experienced variation of composition and synthetic parameters with respect to different applications and use cases [16].

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 1×10^{-3} g/(m²d) with a measurement uncertainty of ± 2 % or at least ± 1×10^{-3} g/(m²d). The measurement area was 78 cm², and the measurement conditions were set to 38°C/90 % RH for all measurements presented in this study.

Cross-section images were obtained by cutting the samples using a 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 HITACHI SEM. Surface roughness was measured using an atomic force microscope (AFM) (TOPOMETRIX Explorer) in non-contact mode on an area of 2.3 µm × 2.3 µm. For larger area scans either an AMBIOS XP-200 surface profilometer averaging 10 line scans with a length of 0.5 mm or a white light interferometry (WLI) (GBS SmartWLI Extended) on an area of 1 mm × 0.75 mm was used.

Optical transmittance, reflectance, and absorption were measured using an ultra violet (UV), visible (VIS), near-infrared (NIR) spectraphotometer Lambda 900 (Perkin Elmer) in the wavelength range between 250 nm and 1300 nm with a 2 nm wavelength step. Total transmittance (T) and total reflectance (R) were measured using an integration sphere including both directed and strayed transmission/reflection. Absorptance (A) was calculated according to: $A = 1 - T - R$ for each wavelength.

Adhesion was 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. Young's modulus of the polymer films (see earlier section) was measured at room temperature according to the standard DIN EN ISO 527-1 using a linear strain test unit described in an earlier study [17].

Plastic dimensional change of the polymer webs after processing in the roll-to-roll wet coating machine was measured as described in [18]. Three rectangles with side lengths of 0.3 m × 0.2 m (shorter dimension was cut in the machine direction) were printed onto each sample prior to passing the machine. Before and after processing, the distance between the parallel lines was measured using an electronic length measurement system with an accuracy of ± 0.01 mm. Each measurement was repeated at several positions on the web. Values given in this paper represent the

Table 1. Comparison of important properties of different fluoropolymer webs with PET and PEN. If no reference is given, the data is based on this study's measurements. Explanation of the symbols: n = refractive index; T_g = glass-transition temperature; T_{vis} = visual light transmission (380 nm–780 nm) weighted with the spectral response of the human eye; $\lambda_{50\%}$ = UV light wavelength with 50 % transmission marking the UV-absorption edge; A_{UV} = average absorption in the UV wavelength range from 280–380 nm; $E_{20°C}$ = Young's modulus in machine direction at 20°C; $E_{120°C}$ = Young's modulus in machine direction at 120°C; R_A = roughness average measured with AFM (indicated with (AFM) in parentheses), and measured on 0.5-mm length (indicated with (LR) in parentheses); R_T = peak-to-peak roughness measured with AFM and either Profilometry (PR) or white light interferometry (WLI), respectively. The annotations "cl" and "hz" refer to clear (cl) and hazy (hz) patches on the PVDF surface that exhibit different surface properties.

	PET	Heat-stabilized PET	PEN PQA1	ECTFE	ETFE	PVDF	PTFE
Thickness of tested web [μm]	75	125	125	50	100	80	30
Structure	$[C_{10}H_8O_4]_n$ phenyl ring	$[C_{10}H_8O_4]_n$ phenyl ring	$[C_{14}H_{10}O_4]_n$ naphthalene double ring	$[(CH_2)_2\text{-}CFCl\text{-}CF_2]_n$	$[(CH_2)_2\text{-}(CF_2)_2]_n$	$[CH_2\text{-}CF_2]_n$	$[CF2]_n$
n @ 550 nm	1.63	1.63	1.68	1.52	1.398 [19]	1.42	1.38 [19]
T_g [°C]	70–78 [9, 20]	70–78 [9, 20]	120 [21]	85 [22]	110 (at 50% TFE) [23]	−40 to −35 (lower glass transition [24])	115 [25]
T_{vis} [%]	87.9	88.9	90,2 (coated)	91.1	93.8	92.1	94.9
A_{UV} [%]	42.1	42.1	58.4	5.6	1.7	12	
$\lambda_{50\%}$ [nm]	314	323	385	< 250	< 250	< 250	< 250
$E_{20°C}$ [MPa]	3700	2500	5000 [9]	1800	820 ± 30	850–1700 [1]	250
$E_{120°C}$ [MPa]	2000 [9]	1200	3500 [9]	-	100 [26]	< 100	-
R_A [nm] (AFM)	0.9	2.1	0.5	7.6–11	4.3	2.1–3.7 (cl) 5–6.9 (hz)	4.9
R_T [nm] (AFM)	10	23	6	63–105	39	19–45 (cl) 46–68 (hz)	40
R_A [nm] (LR)	2.8 (WLI)	-	< 1 (PR)	-	4.6 (WLI)	5.7 (WLI)	12 (PR)
R_T [nm] (LR)	25 (WLI)	-	7 (PR)	-	-	-	88 (PR)

average of each measurement on the same sample. Strain in machine and transverse direction were calculated from the measured distances between the lines (l) by:

$$\Delta l/l = (l_{after} - l_{before})/l_{before}.$$

SPECIFIC PROPERTIES OF FLOUROPOLYMER MATERIALS

A variety of fluoropolymers exist on the market for different applications. This study concentrated on characterizing flouropolymers that were easily available as polymer web and relevant for thin film coating products, for example, in architecture or photovoltaics. Table 1 summarizes and coating-relevant properties of different fluoropolymers in comparison to PET and PEN products. Although most of the given values are material properties of the specific polymer, it is important to note that variations in the properties are possible among different specific commercial products available for each polymer due to differences in the polymer web manufacturing process. For example, surface roughness is strongly dependent on the specific product of the same polymer class, and elastic modulus may alter between web products that have been stretched compared to unstretched films (see below).

One big difference between PET, PEN, and many other polymers is that most fluoropolymers are transparent for ultraviolet light in the relevant wavelength range of 250 nm to 400 nm. As shown in Table 1, commercially available PET films (e.g., DuPont Melinex 401 CW) exhibit a UV absorption edge at 320 nm wavelength. PEN already absorbs UV light with a wavelength of 385 nm and below. Figure 1 com-

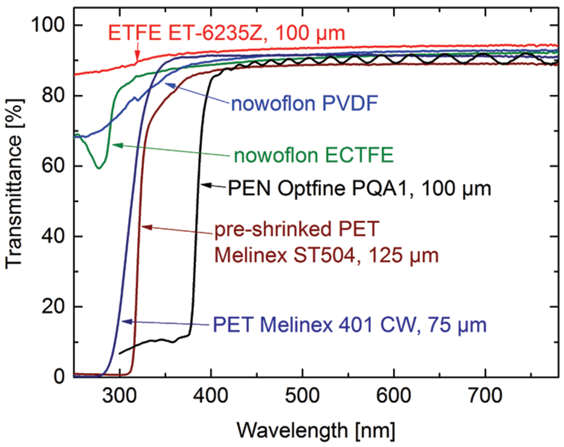

Figure 1. Spectral transmittance of different polymer film products in UV and visible light wavelength range. The interference pattern in the spectrum of the Optfine PQA1 film is caused by an anti-reflective planarization coating on the surface of the PEN product and is not an intrinsic property of the PEN material.

pares the transmission behavior of the polymers in UV and visible wavelength range. Although the UV transparency is not relevant for thin film deposition processes, it indicates better UV stability of the fluoropolymers in application. High UV transparency also may result in the need for a UV blocker or protection layer to potentially protect encapsulated sensitive devices such as organic solar cells against UV light. Refractive index and transmission in visible light range play an important role when thin film coatings on the polymers need to fulfill certain optical requirements or interference colors need to be avoided. For example, a high optical transmission is needed for front-side encapsulation of solar cells whereas thermal insulation coatings ("low-e coatings") in architecture may require a certain color appearance. Compared to PET and PEN, a lower refractive index of fluoropolymers and, hence, a higher transmittance in the visible light range was observed and must be considered in the optical design of thin film coatings for the specific application.

Elastic properties, especially Young's modulus, are very important for thin film coating processes both in vacuum and at atmospheric pressure especially in roll-to-roll processing. Here, a certain web tension is applied to the film for winding through the coating machine. The elastic properties of each polymer web strongly depend on the specific product, chemical structure, and web manufacturing process (e.g., whether the film has been stretched or thermally treated during manufacturing), it is clearly visible from the data in Table 1 that fluoropolymers have a lower elastic modulus than PET and PEN. Fluropolymers require either the use of a much thicker web or lower web tension during roll-to-roll processing to keep strain and induced layer stress low. The elastic modulus of ETFE as well as PVDF is still high enough for processing in typical roll-to-roll vacuum coaters. PTFE exhibits a much lower elastic modulus that is too low for typical roll-to-roll coating setups (see following section). Increasing the web thickness to several 100 µm if not millimeters is often not desired because of material cost and thickness limitations with respect to flexibility during processing and application. The elastic modulus of all polymers mentioned in this study decreases with increasing temperature. At 120°C, ETFE only has an elastic modulus of 100 MPa, which leads to a higher strain at typical web-tension forces used in roll-to-roll processing. Another aspect when considering thin film coating at elevated temperature is the permanent dimensional change or shrinkage of the polymer web at the processing temperature.

Surface roughness is important especially for vacuum coatings for optical, permeation barrier, and electronic applications. Both nanometer scale roughness measured with an AFM and micrometer scale roughness measured with either profilometry or WLI are used to characterize surface quality. While AFM roughness provides information on the "intrinsic" roughness of the web, profilometry and WLI yield information on surface defects, particles (e.g., anti-block particles) and longer-range periodic surface structure that may not be resolved in AFM measurements. Table 1 summarizes the surface roughness of the different polymer web products for the surface side of the web, which has been either denoted by the manufacturer as "good side" or "coating side" or exhibits the lower roughness. While PET and PEN products are available with very low surface roughness in both AFM and WLI scales, commonly available fluoropolymers exhibit higher roughness. This, however, is contradictory to the requirement of a dense amorphous layer structure for reaching a low water vapor transmission rate of barrier layers. Surface roughness of some fluoropolymer products used for this study is also not homogeneous over the surface area. PVDF films show hazy patches on the surfaces that exhibit a higher surface roughness than the optically clear areas. The surface roughness of the ECTFE web also fluctuates strongly with the different measurement positions on one sample. A roughness range for the two materials is therefore given in Table 1 instead of a single roughness value. The surface roughness does not mainly represent a property of the polymer itself but includes the web manufacturing process. On most fluoropolymer webs a planarization layer is preferred to improve the surface smoothness for subsequent deposition of permeation barrier or transparent electrode layers.

COATING RESULTS AND DISCUSSION

Layer Adhesion on Fluoropolymer Substrates

Most fluoropolymers are known to have low adhesion to both organic and inorganic coating. Table 2 shows the adhesion forces of ZTO, Al_2O_3, and ORMOCER layers on ETFE and PVDF in comparison to PET. Surprisingly, reactively sputtered zinc-tin-oxide shows sufficient adhesion on both the ETFE and the PVDF substrates when deposited directly onto the polymer surface without any further pre-treatment. Adhesion forces (Table 2) are almost as high as on PET. However, the numeric values do not represent the adhesion force between the ZTO and the fluoropolymer but are between the ZTO and the lamination adhesive used for the test. Adhesion failed first at the interface to the adhesive. An ORMOCER layer shows a peel force larger than 10 N/cm on all three tested substrates. In contrast to that, the typically used permeation barrier material aluminum oxide (Al_2O_3) exhibits very low adhesion on both ETFE and PVDF. Adhesion forces were not measurable in the 90° peel test.

Adhesion Promotion for Al_2O_3 Layers

Plasma surface treatment of the ETFE (by using a Linear Ion Source (Advanced Energy Inc.) in an oxygen plasma at 75 W power or by adding an adhesion promotion layer between ETFE and the Al_2O_3 layer significantly increases adhesion of Al_2O_3 to ETFE to 6 N/cm or higher (Figure 2). The peel-test adhesion failed at the interface between the adhesive used to prepare the peel test samples instead of at the interface between the substrate surface and the Al_2O_3 layer. The measured peel force was to 6 N/cm or higher – resulting in adhesion failure between the sample and the lamination adhesive used for mounting the sample to the peel-test carrier film. In the plasma treatment, the adhesion promotion is a result of surface roughening, chemical activation and surface contamination reduction in the reactive oxygen plasma [26]. Long-term investigation of adhesion (e.g., potential adhesion failure after a certain period of sample storage) was not studied but must be taken into account when considering coated fluoropolymers for any application with a long expected lifetime such as solar module front sheets or low-e coatings for membrane roof elements.

Table 2. Adhesion forces of ZTO, Al_2O_3, and ORMOCER layers on different polymers. For all values given for ZTO and ORMOCER® adhesion failure took place between the peel-test adhesive and the coating instead of between the polymer and the coating. The numbers in the table therefore indicate a minimum adhesion force.

Substrate	Layer material	Layer thickness [nm]	Minimum adhesion force [N/cm]
PET Melinex 400 CW	ZTO	100	> 7.5
	Al_2O_3	100	10.7
	ORMOCER	1000	> 10
ETFE	ZTO	50	> 7.5
	ORMOCER	1000	11.5
	Al_2O_3	100	< 0.5
ECTFE	ZTO	160	> 7.5
	ORMOCER	1000	> 10
PVDF	ZTO	80	> 7
	Al_2O_3	100	< 0.5
	ORMOCER	1000	10.3

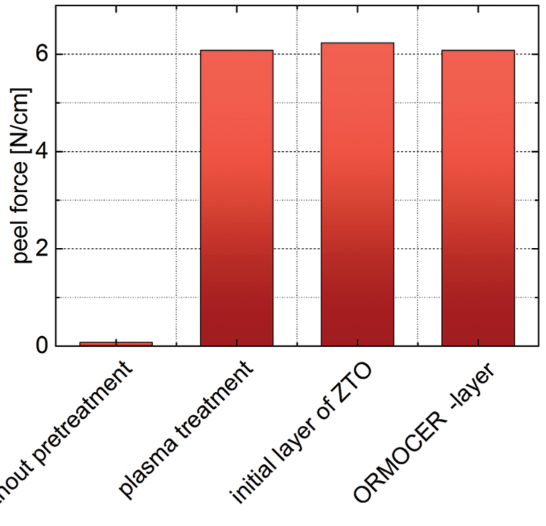

Figure 2. Adhesion of sputtered Al_2O_3 on ETFE comparing different ETFE surface pretreatment techniques.

Surface Roughness and Planarization Effect with ORMOCER

As mentioned earlier, surface roughness is a critical aspect of fluoropolymer substrates when being used for coating of oxide permeation barrier layers. The ORMOCER layer is intended to be used as a planarization layer to provide a smooth surface for subsequent permeation barrier layer deposition. Figure 3 shows the AFM surface roughness of the uncoated ETFE web and the coated ETFE surface after deposition of a 6 µm thick ORMOCER layer. The roughness is reduced significantly after applying the ORMOCER layer. The planarizing effect is increased with increasing ORMOCER thickness. However, as shown in Figure 4, a 2 µm thick ORMOCER layer is sufficient to cover the fibrous ETFE surface (Figure 4 left image) and to allow deposition of smooth ZTO barrier layers on top.

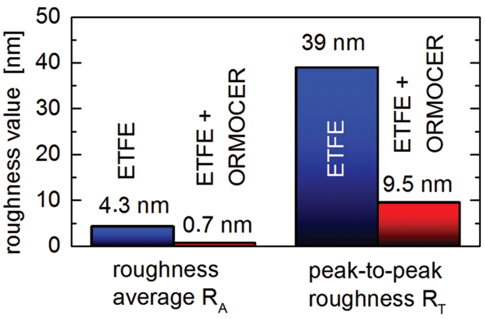

Figure 3. Comparison of AFM surface roughness of ETFE ET-6235Z before and after coating with a 6-μm-thick ORMOCER layer

Water Vapor Permeability of Vacuum-Coated Single Layers on Different Fluoropolymers

Earlier studies demonstrated that water vapor permeability of oxide single layers strongly depends on the surface quality and roughness of the polymer substrate [10]. Figure 5 compares the water vapor permeability (at 38°C/90 % RH) for ZTO layers on ETFE and PVDF substrates to values measured on PET Melinex 401 CW film. In spite of the high surface roughness, ZTO shows, at high thickness, even lower WVTRs on ETFE compared to the PET substrate but requires a higher layer thickness for reaching the same low WVTR as on PET. The reason for this behavior is the higher surface roughness of the ETFE. Reasonably low WVTR was also reached on PVDF in spite of the inhomogeneous surface roughness.

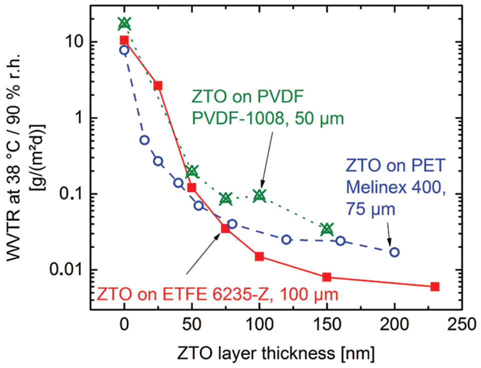

Figure 5. Comparison of water vapor transmission rates of ZTO layers on PET, ETFE, and PVDF.

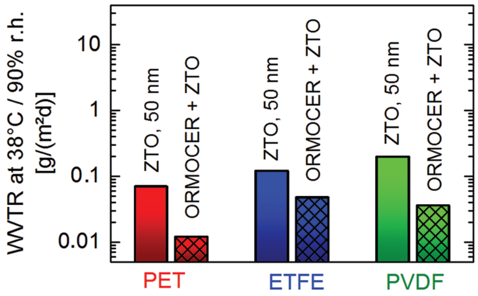

Figure 6. Effect of a 1.6-μm-thick ORMOCER planarization layer on the WVTR of ZTO (50-nm thickness) on different substrates.

As shown earlier, an ORMOCER layer planarizes the polymer surface to allow improved ZTO layer quality. Figure 6 shows the WVTR of ZTO-coated ETFE, PVDF, and PET with and without an ORMOCER layer between the substrate and the ZTO. In all cases, the ORMOCER planarization layer leads to a lower WVTR of the coated film. The lowest WVTR is still reached on Melinex 401 CW, indicating that the planarization effect on the fluoropolymers might still be improved with using higher ORMOCER thickness. However, a WTVR below 4 × 10^{-2} g/(m²d) may be reached even on ETFE and PVDF substrates with a ZTO layer thickness of 50 nm. The WVTR of a 50 nm thick ZTO layer on an ORMOCER on a planarized ECTFE substrate was $6{\cdot}10^{-2}$ g/(m²d), thus being in the same range as on ETFE and PVDF. The ORMOCER planarization potentially reduces

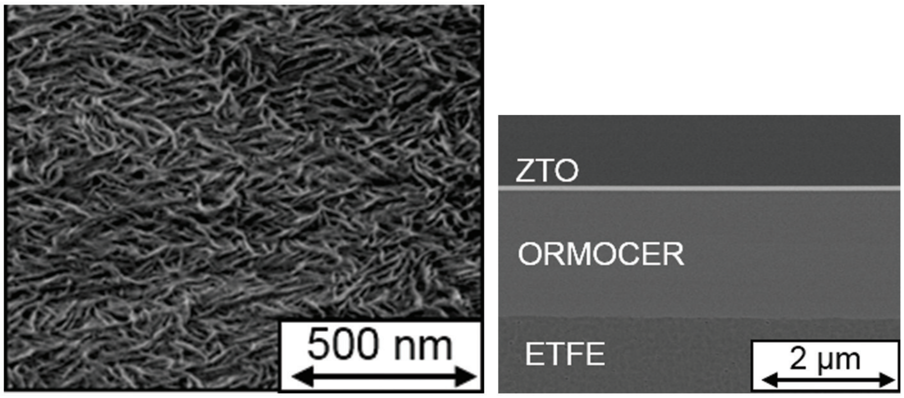

Figure 4. Left image shows SEM surface image of an untreated ETFE surface, showing fibrous texture. Right image shows SEM cross-section images of a two-layer stack of ORMOCER (2 μm) + ZTO (50 nm) on ETFE.

the influence of the surface roughness of the bare polymer web with respect to the permeation barrier properties of ZTO coatings on the polymers.

Mechanical Behavior During and After Processing

Earlier studies demonstrated that the best permeation barrier performance on PET and PEN substrates is achieved with a multilayer stack of at least two ZTO barrier layers separated by an ORMOCER interlayer [15]. The interlayer covers and planarizes defects on the substrate and improves mechanical flexibility in the whole system due to the fact, that a thinner oxide barrier layer may be used instead of one thick single oxide layer. Adding another ORMOCER layer after ZTO deposition on fluoropolymer substrates requires special attention to the low elastic modulus and dimensional stability of the substrate material [18]. The importance of dimensional stability and elastic properties are demonstrated when elastic films are strained by tensile forces such as web tension in roll-to-roll processing. This must be taken into account when coated polymer webs need to be processed again in roll-to-roll, for example, in deposition of additional layers or lamination steps. Inorganic oxide coatings such as ZTO, Al_2O_3, or indium-tin-oxide (ITO) only withstand a certain strain until crack formation is observed. As shown in earlier studies on PET substrates, ZTO single layers have a crack-onset-strain (elongation at which first cracks are observed in an optical microscope) of 0.7 % at a layer thickness of 150 nm; a thinner layer (50-nm thickness) shows first cracks at 1.4 % relative elongation [28]. On the other hand, shrinkage of the polymer web leads to buckling of the layers due to compressive stress. Assuming room temperature operation, the elastic moduli given in Table 1 would allow for using web tension of up to 26 MPa (meaning 800 N web tension force on a 75 µm thick, 400 mm wide PET roll) before cracking a 160 nm thick ZTO layer at 0.7 % strain. On ETFE about 5 MPa web tension (approx. 200 N tension force for 100 µm thick ETFE at 400 mm web width) may be used, and strain must stay below 0.7 % to avoid cracking of coatings. ECTFE is more desirable over ETFE or PVDF because of its higher elastic modulus. PTFE, however, requires a reduction of web tension to 1.6 MPa to keep strain under 0.7 %. The same is true for fluorinated ethylene propylene (FEP) substrates (having an elastic modulus of 450 MPa); 450 MPa elastic modulus allows a maximum web tension of 3 MPa. Such low tensile forces often cannot be used in typical commercially available roll coating machines.

In many cases, it is desirable to operate at higher substrate temperatures in the 100°C range to gain higher coating quality and denser layers (e.g., in PECVD SiN coating for barrier application [29] or ALD processes for Al_2O_3 deposition [30]) or for thermal-curing wet-coated lacquers. Thermal curing of ORMOCER was done at 120°C in this study. At 120°C, the reduced elastic modulus of the polymer webs was a critical issue allowing PET a web tension of 6.8 MPa and ETFE a web tension of less than 0.7 MPa. This kept film strain below 0.7 %, taking into account the elastic modulus of 100 MPa.

In addition to elastic strain under tension, plastic (meaning permanent dimensional changes) were observed for polymer webs when tensile forces and elevated temperature were applied to the film in a roll-to-roll coating process. This is especially true when the glass-transition temperature is exceeded during processing for a certain time, causing a re-orientation and relaxation of crystallites in the polymer material. Based on the results of an earlier focused study on the plastic dimensional change [18], different polymers were processed in an atmospheric roll-coating machine at different temperatures and web tension settings, and then plastic deformation was measured afterwards.

Figure 7 shows the relative permanent dimensional change of the ETFE web after processing at different conditions. Positive values indicate strain/elongation, and negative values indicate compression/shrinkage. No significant permanent dimensional change was observed on any substrate as long as the processing temperature was 80°C or less. At

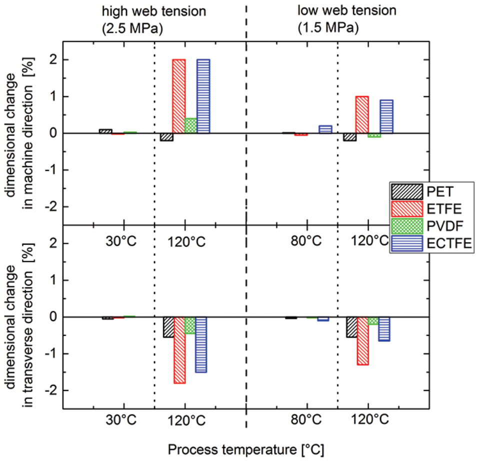

Figure 7. Dimensional change of PET Melinex 400 CW in comparison to the fluoropolymers ETFE, ECTFE, and PVDF after processing in a roll-to-roll coating machine at atmospheric pressure and using different web tension forces and different operation temperatures. The upper diagrams show the length change in machine direction, the lower diagram the width change (transverse direction). Positive values indicate a strain/elongation; negative values indicate a compression/shrinkage

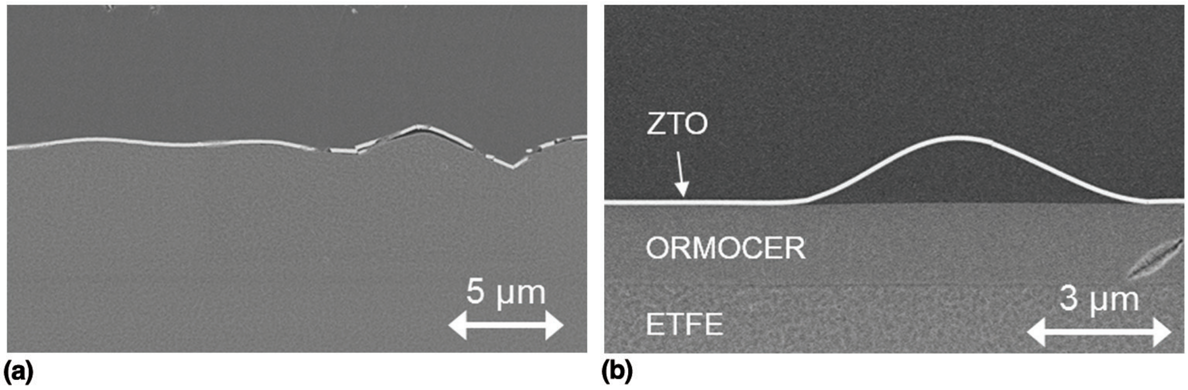

Figure 8. SEM cross-section images of ZTO on ETFE show failure mechanisms: (a) cracking and (b) buckling after subsequent thermal processing in roll-to-roll at a web tension of 2.5 MPa.

120°C, however, strong shrinkage was observed in the transverse direction for PET Melinex 400 CW, ETFE, and ECTFE. The shrinkage was constant for PET, but shrinkage for the fluoropolymers were dependent on the tension of the web. For PET, the shrinkage is independent from the web-tension. However, all three fluoropolymer films show much higher shrinkage after applying higher web-tension. In machine direction, PET also exhibited a small shrinkage while ETFE showed plastic elongation of up to 2 % at 2.5 MPa web tension. While any observed dimensional change for PET was below 0.7 %, thus not damaging ZTO layers, ETFE deformation was in a range critical for 50-nm-thin ZTO layers reaching strain values above 1.4 % when the web tension was higher than 1.5 MPa. Similar to pre-shrunk polymers such as the Melinex ST504 film (which was thermally pretreated to avoid shrinkage in processing [9]), the plastic deformation occurred only at the first exposure to high temperature and tension in the machine, while repeating the test did not lead to additional elongation or shrinkage of the film. A more detailed analysis of the dimensional change of different polymers while processing in a roll-to-roll wet coating machine is given in [18] and [31]. Elastic (reversible) deformation of the substrate under influence of temperature and strain still occurred, potentially damaging the oxide coating. Water vapor transmission rates of ZTO coatings that had been subsequently processed at 120°C and high web tension were thus increased compared to coatings that were measured directly after ZTO deposition (see multilayer barrier results below). The SEM cross-section images given in Figure 8 clearly depict the effect of the dimensional change of the substrate to ZTO barrier layers which led to barrier performance loss. As visible in the left image of Figure 8, the ZTO layer cracked after tensile stress was applied (e.g., in machine direction). The right image shows an example of buckling resulting from high compressive stress.

Multilayer Permeation Barrier Stacks on ETFE

Taking into account the process parameter limitations described earlier, multilayer permeation barrier stacks were applied on ETFE webs in roll-to-roll processes. At first, only a second ORMOCER layer was applied to the ETFE/ORMOCER/ZTO stack at the low web tension configuration (1.5 MPa) processed at different ORMOCER curing temperatures.

Figure 9 shows that the water vapor transmission rates of the three-layer stack (ETFE/ORMOCER/ZTO/ORMOCER) is dependent on the curing temperature of the second ORMOCER layer. The first ORMOCER layer was cured at 120°C. That means that the substrate had already been processed in the machine, thus reducing plastic deformation (permanent shrinkage) in the second run through the machine. While 50-nm-thick ZTO layers show a low WVTR even after ORMOCER curing at 120°C, the 160-nm-thick ZTO layers were damaged with the 80°C processing temperature of the second ORMOCER layer, resulting in a higher WVTR. Similar results were observed on the 80-µm-

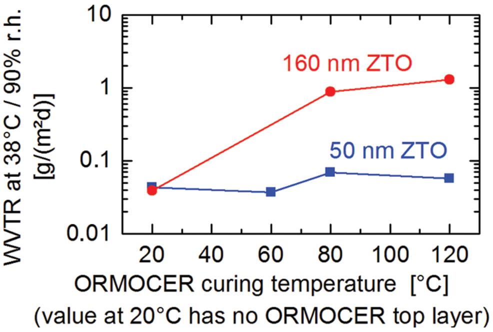

Figure 9. Water vapor transmission rates (WTVR) of a layer stack ORMOCER/ZTO/ORMOCER on 100 µm thick ETFE shows dependence on the ORMOCER curing temperature at a web tension of 1.5 MPa.

thick PVDF substrate. Water vapor permeability of a 160 nm thick ZTO layer on planarized PVDF increased from 0.038 g/(m^{2}d) to 1.64 g/(m^{2}d) after ORMOCER deposition at 120°C. Visible cracks were observed after exposing the ZTO-coated PVDF to 120°C. Adding another ZTO barrier layer may reduce water vapor transmission rate again.

Table 3 summarizes the WTVRs of multilayer stacks on different substrates with one or two ZTO layers. Two different winding configurations in the vacuum coating machine and in the wet coating machines were compared. First, the typical process parameters for PET and PEN coating were a web tension of 2.5 MPa for wet coating and of 8.3 MPa for vacuum coating. These settings were compared to web winding parameters according to the experimental results described in this paper, specifically meaning a web tension of 1.5 MPa in wet coating and 25 MPa in vacuum coating. ORMOCER curing temperature was kept at 120°C to ensure proper crosslinking of the ORMOCER. Low water vapor transmission rates at the measurement limit of the available permeation measurement system were achieved with 150-nm-thick ZTO layers in a multilayer stack on both PET and PEN. Calcium test measurement on the layer stacks on those substrates determined a WVTR of less than 2×10^{-4} g/(m^{2}d) at 38°C/90 % RH as demonstrated in an earlier study [32]. Applying the same layer stack on ETFE resulted in a high water vapor transmission rate of 0.79 g/(m^{2}d) because of damage to the first ZTO layers caused by the earlier mentioned mechanical stress in subsequent processing. Damage occurred during the ORMOCER and ZTO layer deposition, regardless of high or low web tension used during processing. Elastic deformation during processing resulted in cracking of the ZTO layers, thus increasing the WVTR again.

However, very low water vapor transmission rates were observed in multilayer stacks with 50 nm thick ZTO layers on ETFE. A winding configuration with low web tension forces yielded the lowest WVTR of less than 1×10^{-3} g/(m^{2}d) in a four-layer stack: ETFE ORMOCER/ZTO/ORMOCER/ZTO. That WVTR is similar compared to the same barrier layer stack on a PET substrate. However, both almost touch the limit of detection of the coulometric permeation measurement device, thus hiding potential differences in a lower WVTR range. This result shows that web tension and mechanical stress to the layer stack is low enough to avoid damage to the 50-nm-thick ZTO layer – finally demonstrating successful roll-to-roll processing and barrier layer deposition on a fluoropolymer.

CONCLUSION AND OUTLOOK

This paper demonstrated that both wet chemical and vacuum coating of planarization and permeation barrier layers is possible on fluoropolymer substrates. An ORMOCER

Table 3. Water vapor transmission rates of multilayer permeation barrier stacks prepared under different roll-to-roll processing conditions. ORMOCER is abbreviated with "ORM"; ORMOCER thickness was ≈ 1.3 ± 0.3 µm in all samples described below. The curing temperature was 120°C in any setting. The term "high" in the web tension column refers to the following processing conditions: ZTO cooled from backside to 10°C; web tension 8.3 MPa; ORMOCER curing temperature 120°C at 2.5MPa web tension. The term "low" refers to 2.5 MPa web tension at 10°C for ZTO and 1.5 MPa web tension at 120°C for ORMOCER coatings.

Substrate	Layer stack	ZTO thickness [nm]	Web tension	WVTR @ 38°C / 90 % RH [g/(m^{2}d)]
PET	sub / ORM / ZTO / ORM	50	high	0.03
		150		0.01
	sub / ORM / ZTO / ORM / ZTO	50	high	0.004
		150		≤ 0.001 (limit of detection)
PEN	sub / ZTO / ORM / ZTO	150	high	≤ 0.001 (limit of detection)
ETFE	sub / ORM / ZTO	50	high	0.04
		150	high	0.09
	sub / ORM / ZTO / ORM	50	low	0.05
		50	high	1.6
		150	low	0.8
	sub / ORM / ZTO / ORM / ZTO	50	high	0.04 [10]
		50	low	0.001
		25	low	0.008
		150	low	0.79

planarization layer as well as ZTO permeation barrier layers were successfully applied to ETFE and PVDF films with a good adhesion force higher than 10 N/cm. Both ZTO and ORMOCER may be used as adhesion promotion layers for other vacuum-coated layers such as Al_2O_3 or potentially other conductive layers to improve the adhesion of these materials on the fluoropolymer surface, thereby enabling not only permeation barriers but also transparent electrodes or optical layer stacks on ETFE and other fluoropolymers webs.

Elastic properties of the fluoropolymers – especially a low elastic modulus at elevated temperature and shrinkage – were identified as critical aspects for roll-to-roll processing. With optimized processing parameters, however, permeation barrier layer stacks were successfully applied on ETFE web with water vapor transmission rates of 1 × 10^{-3} g/m²d at 38°C/90 % RH. These process parameters comprise low web tension and lower sputtered layer thickness with higher crack-onset strain, resulting in the dimensional change of the ETFE during coating that does not lead to cracking of the sputtered layer. The WVTR of the multi-layer stacks on ETFE are comparable to the same layer stacks on PET substrates. However, the WVTR touches the limit of detection of the coulometric parameters. More accurate permeation measurements and an optical calcium test on the layer stacks on ETFE are the next step. Better measurements will help determine the influence of different substrates in the multi-layer barriers. This will help understand the role of substrate defect patterns in the multi-layer barrier stacks.

One possible method to improve dimensional stability of the ETFE is thermal stretching of the web prior to thin film coating. As investigated in more detail in another study [33], uniaxial stretching of the ETFE film to a factor of 6:1 resulted in a significant increase in the elastic modulus up to 6000 MPa (see Figure 10). That value is even higher than for PET or PEN and strongly reduces strain when applying web tension in roll-to-roll processing. However, the elastic modulus at higher temperature (staying below the stretching temperature of 140°C for this experiment) still has to be measured and coating experiments have to be done to fully evaluate the influence of uniaxial as well as biaxial film stretching on the behavior of the polymer web in thin film coatings. Shrinkage of the stretched film under influence of temperature may also be an issue to consider when preparing permeation barrier coatings on stretched ETFE substrates.

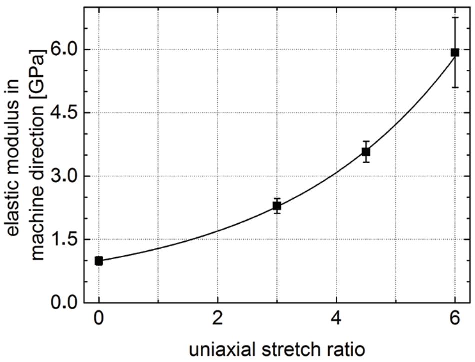

Figure 10. Young's modulus of ETFE in the machine direction shows the dependence on the stretching ratio by uniaxial stretching of a 300-µm-thick ETFE film in the machine direction.

With respect to application, long-term stability of the functional properties of the coated fluoropolymer webs still has to be demonstrated, especially for typical requirements for an outdoor environment and simulated aging tests such as temperature cycling tests, damp-heat test, and UV tests. Furthermore, the long-term flow behavior of many fluoropolymer webs has to be considered and evaluated for the coated films in more detail before a final statement for applicability such as front-side encapsulation sheets for solar cells may be given.

Demonstrating successful deposition of permeation barrier stacks on ETFE and PVDF was the first step to market penetration of coated fluoropolymer webs for functionalization of membrane roofs and facades with flexible thin-film solar cells, thermal insulation and solar control functionality, and flexible thin film electroluminescent and OLED lighting panels as well as electrochromic devices.

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FOR MORE INFORMATION:

John Fahlteich, Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP, Winterbergstraße 28, 01277 DRESDEN, Germany, john.fahlteich@fep.fraunhofer.de, +49/351 258 61 36