More than just Protection

Surface Functionalization of Fluoropolymer Films for Exterior Applications

Coated polymer films are widely used in everyday life. For exterior applications, they have to withstand particular stresses, such as UV radiation and extreme temperature variations, and are often required to endure very long periods of service. To meet these challenges, a functionalization concept to produce weathering-resistant films has been developed. It is the first step towards integrating solar cells or lighting elements into flexible membrane roofs and façades.

Outdoor weathering test rig on the roof of the Technical Center at the Fraunhofer FEP in Dresden (figures: Fraunhofer FEP)

Flexible electronic construction elements such as thin-film solar cells or flexible light sources and displays based on organic light-emitting diodes (OLED) open up many new applications and allow greater design freedom. For example, solar cells or lighting elements can be integrated into handbags or clothing and flexible screens can be developed for cell phones or television sets. Flexible electronics can also be used in large-area building façades, roofs, stadiums or function halls, where, for example, solar cells can turn light into electrical energy.

Such flexible electronic devices must be protected from environmental effects by encapsulation. In particular, protection is required against corrosive gases such as moisture and oxygen, UV radiation, and mechanical stresses due to e.g. hail. The standard material used to encapsulate solar modules is glass, which has a good protective effect against the above stresses. The disadvantages of glass are its relatively high weight and lack of flexibility and formability. These disadvantages can be eliminated by switching to film-based encapsulation with a coated functional film. »

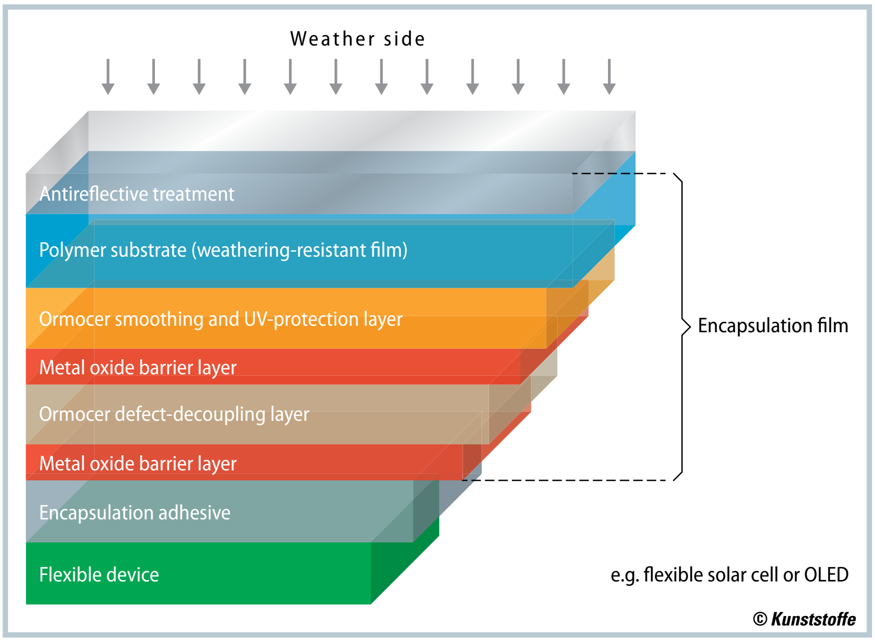

Fig. 1. System structure for front encapsulation of flexible electronic devices with a coated polymer film

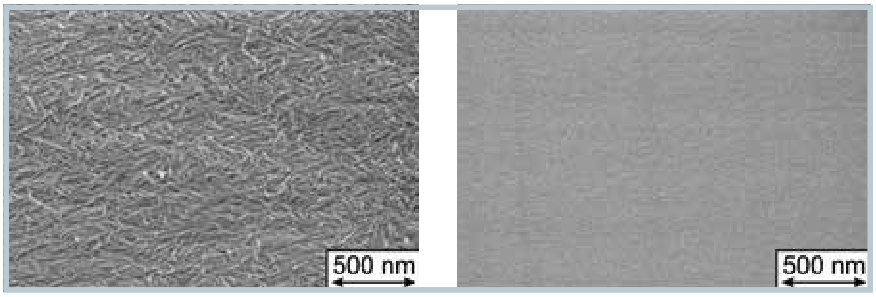

Fig. 2. Scanning electron microscopy image of the surface structure of an ETFE film (left) and surface of a coated ETFE film after application of an Ormocer/ZTO double layer (right)

Production of the Functional Film

Scientists at the Fraunhofer Institute for Silicate Research (ISC), Würzburg, Germany, the Fraunhofer Institute for Process Engineering and Packaging (IVV), Freising, Germany, and the Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology (FEP), Dresden, Germany, have jointly developed a process for the production of functional films that can be used to encapsulate flexible electronic devices and solar cells. **Figure 1** shows the structure of a functional film integrated into a flexible solar module. The antireflective-treated film surface is on the weather side. Depending on mechanical stability requirements, a scratch-resistant coating is also possible instead. The functional surface coating on the film faces the device. The coating has the task to planarize the film surface as well as provide UV protection and, through a barrier layer system, prevent water vapor and oxygen permeation through the functional film.

The encapsulating film is based on a multilayer system of hybrid polymer layers and at least one metal oxide layer, which is applied by vacuum coating [1]. Inorganic-organic hybrid polymers are used in the form of Ormocer layers produced by the sol-gel process with properties tailored to the specific application [2]. They can, for example, be applied to the surface as thermally or UV crosslinkable lacquer in a wet coating process. The layers planarize and cover surface and layer defects in the barrier system. Ormocer coating is done in a continuous roll to roll process.

The metal oxide layers form a barrier against the diffusion of water vapor and oxygen. The materials generally used are zinc-tin oxide (ZTO – Zn_2SnO_4) or aluminum oxide (Al_2O_3), which are deposited by reactive dual magnetron sputtering in vacuum. Magnetron sputtering is a common process in industry for large area roll-to-roll coating of polymer films for different applications. .

For the barrier layer system, Ormocer layers and ZTO layers are applied alternately to a polymer film. Previous research work concentrated on applying the layer stack to substrate films produced from the frequently used polymers polyethylene terephthalate (PET) and polyethylene naphthalate (PEN). With a layer structure as shown in **Figure 1**, water vapor transmission rates (WVTR) below $5 \cdot 10^{-5}$ g/(m^{2}d) are achieved on these substrates at room temperature and 50 % relative humidity. In comparison to an uncoated film, the water vapor permeability is reduced by a factor of 100,000 though the coating. If these functional films are to be used outdoors, PET and PEN are unsuitable because of their limited UV stability and moisture resistance. Just a few months in an outdoor weathering test (**Title figure**) in Central Europe is sufficient to destroy a functional film based on PET or PEN.

Substrates for Exterior Use

Through the use of weathering-resistant polymers as substrate, functional films can have a much longer service life. Fluoropolymers are a suitable material class here, with ethylene tetrafluoroethylene (ETFE), in particular, being used for membrane roofs, e.g. in stadiums or function halls [3, 4]. Coating fluoropolymer films with barrier layers or other functional thin layers is a particular challenge in view of the characteristic properties of fluoropolymers. They have a much lower elastic modulus than the standard substrates PET and PEN. A low elastic modulus results in higher film strain under mechanical tensile stress, such as occurs in a roll to roll process as a result of the web tension. This strain damages layers already applied. Process temperatures above 100 °C, which are required for crosslinking Ormocer coatings, exacerbate this problem. While typical commercially available ETFE films have an elastic modulus of around 1,000 MPa at room temperature (4 times lower than that of a standard PET film), their elastic modulus at 120 °C is only 100 MPa. This low value places enormous demands on the roll to roll process and the web winding system used for continuous substrate movement. Another point to keep in mind is the low adhesion of many layer materials on fluoropolymer surfaces. In the vacuum coating process, the high surface roughness leads to porous layer growth, resulting in higher water vapor permeability and hence lower barrier effect than is the case on PET or PEN.

Barrier Layer System with Fluoropolymers

As part of a research project funded by the German Federal Ministry of Education and Research BMBF ("flex25" – ref. no. 03V0224), Fraunhofer researchers are working to apply the technology described above to the production of barrier layer systems on fluoropolymer substrates. To accomplish this, the first step is to achieve sufficient layer adhesion. Both Ormocer after Corona pretreatment and ZTO layers have very good adhesion to the fluoropolymer films ETFE and PVDF. The bond strength values (measured according to standard IPC-TM-650) are higher than 10 N/cm for both the selected Ormocer coatings and the ZTO [5]. They considerably exceed the bond strength values of other frequently used layer materials, such as aluminum oxide, which has a bond strength of less than 1 N/cm on ETFE.

The rough surface of the ETFE film can be planarized by applying an Ormocer coating. Even with a coating of the hybrid polymer just a few microns thick, a reduction in the arithmetic roughness mean (measured by atomic force microscopy) of over 75 % from 4 nm to less than 1 nm was demonstrated. **Figure 2** left clearly shows the textured rough surface of a commercially available ETFE film. The picture on the right shows the smoothing effect of the Ormocer coating, which enabled a very smooth and flawless ZTO layer to be deposited on the hybrid polymer.

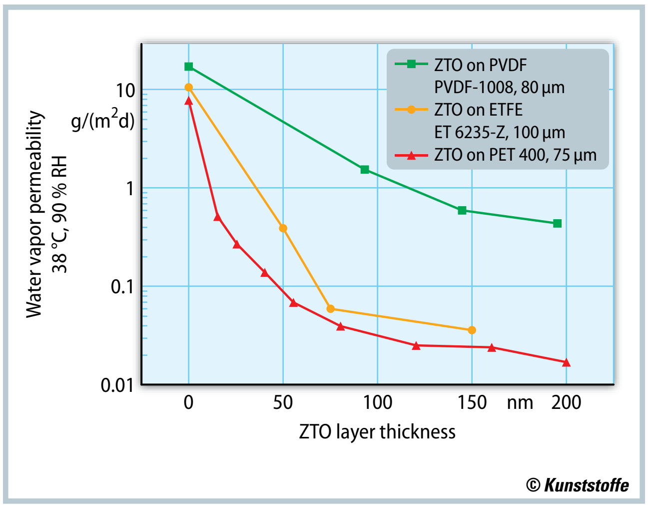

Fig. 3. Comparison of the water vapor permeability of ZTO layers on different substrates

Even without planarization, it is possible with a single sputtered ZTO layer to reduce the moisture vapor permeability of ETFE to a value less than 0.05 g/(m²d) at 38 °C and 90 % relative humidity. This is 100 times lower than the comparative value for an uncoated ETFE film and only slightly higher than the value for a ZTO layer of equal thickness on a PET film (**Fig. 3**). The achievable barrier effect is highly dependent on the specific substrate material/product used and on its surface properties. On polyvinylidene fluoride (PVDF), the moisture vapor permeability values of ZTO layers are much higher than on ETFE and PET. But if the surface is planarized with an Ormocer layer, similarly low moisture vapor permeability values are measured with ZTO layers (0.04 g/(m²d) with 50 nm ZTO at 38 °C/90 % relative humidity). The smoothing layer reduces the influence of the polymer surface on the barrier effect of the metal oxide layer.

It is necessary to adapt the coating process to the particular mechanical properties of the fluoropolymer films to apply a layer system. Ormocer coating is carried out using a reverse gravure coating process followed by thermal crosslinking at a temperature of 120 °C. Because of the low elastic modulus of ETFE at 120 °C, the web tensions typically used in the roll to roll coating process lead to a relative elongation (strain)of the »

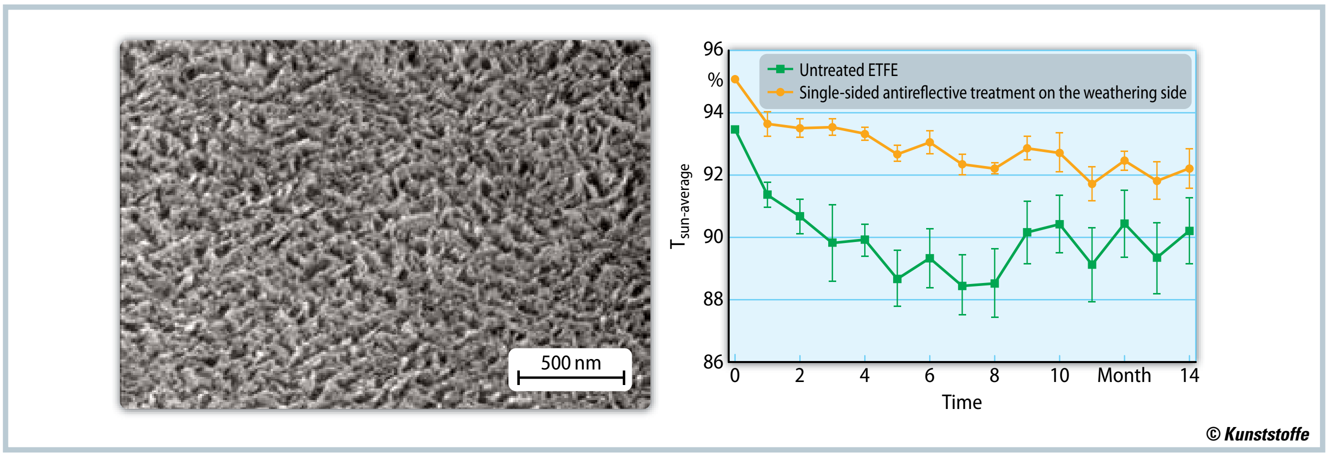

Fig. 4. Scanning electron surface micrographs of ETFE film after antireflective treatment by plasma-assisted nanostructuring (left), change in the light transmission of the film given single-sided antireflective treatment in an outdoor weathering test over a period of 14 months (right). The antireflective treatment was on the weather side

film of up to +2 % [6]. With this degree of stretching, a 100 nm thick ZTO layer exhibits significant cracking and loses its moisture barrier effect. Plastic deformation, such as heat shrinkage of the film, exacerbates this problem. Nevertheless, it has been possible to adapt the roll to roll Ormocer coating process so that the underlying ZTO layers are not damaged by stretching or shrinkage of the ETFE film. For a layer system consisting of an ETFE/Ormocer smoothing layer/50 nm ZTO/Ormocer covering layer, a moisture vapor permeability of $0.04\,g/(m^2d)$ was measured at 38 °C and 90 % relative humidity. By applying additional ZTO/Ormocer double layers, the moisture vapor permeability can potentially be further reduced.

Nanostructuring of the Surface

Besides low moisture vapor permeability, the film is required to have a light transmission value in the range of the solar glass reference material, particularly if the film is being used as front encapsulation for solar cells. To achieve this, light transmission can be increased by antireflective treatment of the outside surface. This is accomplished in the “flex25 project” by plasma-assisted nanostructuring of the surface. With randomly arranged nanostructures (**Fig. 4, left**), continuous transition of the refractive index on the film surface is obtained, which makes the film optically antireflective and increases light transmission. The process is based on treatment (etching) of the film surfaces with pure oxygen plasma. The plasma source is a dual magnetron system, which can be scaled up for large film widths. The potential of this technology becomes clear if we consider the effect of giving both sides of the fluoropolymer film an antireflective treatment. This enables a maximum light transmission of 98.7 % to be achieved at 600 nm wavelength [7]. With the single-sided treatment of the film surface used here, a transmission value of up to 95.1 % can be obtained (based on the visible emission spectrum of the sun (T_{sun})).

A single antireflective treatment on the outer weather side is used for front encapsulation of flexible solar cells. The antireflective surface is stable for a long period of time in the outdoor weathering test. Although **Figure 4 right** shows that the light transmission of the film is reduced over time, the difference between the antireflective and non-antireflective films is maintained throughout the test period.

Long-term outdoor weathering tests on the complete functional film are presently being conducted on the roof of the Fraunhofer FEP Technical Center (**Title figure**). The results described here show that surface functionalization of fluoropolymer films can be successfully carried out by both wet chemical and vacuum coating. With the technology presented here, not just permeation barrier layers but also electrodes, optically effective or decorative layer systems, and scratch-resistant coatings can be applied to fluoropolymer films. This not only enables encapsulation of flexible solar cells but also opens up the possibility of ETFE-based lighting systems, e. g. with organic light-emitting diodes, or electrically dimmable systems with electrochromic layers.

Outlook and Examples of Use

In Germany alone, several hundred buildings have been constructed with membrane roofs and façades produced from fluoropolymer films such as ETFE. If just the roof of the Olympiastadion in Berlin, Germany, which has a 27,000 m^2 ETFE membrane roof area, was equipped with thin-film solar cells, a maximum output of 2.7 MWp could be achieved with only 10 % module efficiency. This amounts to nearly 3,000 megawatt hours per year being enough electrical energy to supply about 750 households with electricity for a year. The façade and roof of the Allianz Arena in Munich, Germany, are constructed from ETFE air cushions covering a total area of 68,000 m^2, which could potentially be used for power generation. To accomplish this, the Fraunhofer researchers are working on the next step of adapting the new technology to encapsulate flexible electronic devices with functional films and applying the devices directly to the surface of the coated ETFE film (**Fig. 1**). The vast areas of ETFE-based membrane roofs offer considerable market potential for integrated flexible electronic devices and the associated technologies. ■

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