

Fluorothermoplastics offer flexible film solutions

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More than 70 years after the discovery of polytetrafluoroethylene (PTFE), fluoropolymers have become well established as an extremely useful material family in a variety of technical applications. In addition to PTFE itself, which cannot be processed with many of the conventional methods, utilised in plastics technology, a whole series of fluorothermoplastics that are flexible to handle has gained a place in everyday life. In film applications they stand out among other things by exceptional resistance to tear propagation and chemical resistance. Most visible for many consumers are fluorothermoplastic films in outdoor applications: PTFE-derived fluorinated plastics such as ethylene-tetrafluoroethylene (ETFE) are used among other things in photovoltaic systems and architecture. Here they convince, for example, due to their high robustness and self-cleaning properties. Another advantage is the considerably lower weight compared to glass, which enables the design of more filigree load bearing structures or permits them in the first place. Not least, these weather resistant films allow the realisation of very courageous and aesthetically pleasing architectural ideas. Also, the problem of heat build-up under transparent fluorothermoplastic roofs can now be solved, thanks to the new, multilayer optical films.

1 Introduction

Fluoropolymers can be classified into three groups: fluorothermoplastics (FTP), fluoroelastomers (FE) and polytetrafluoroethylene (PTFE). The exceptional position of PTFE results from its extremely low melt flow index (MFI): The polymer doesn't melt; instead, it merely transforms itself into a transparent, non-flowing gel when exposed to temperatures above around 330 °C. Special technologies must therefore be used to process this material, for example compression moulding, isostatic moulding, ram or paste extrusion. Films and fabrics can be made from PTFE, using special process technology (**fig. 1**).

By contrast, fluorothermoplastics – despite extremely high melting points in some cases – exhibit melt flow indices of 1 to 40 g/10 min. This means that they are suitable for a whole series of processing methods used with other thermoplastic materials [1]. Ultimately, these polymers have been developed with the goal of harmonising the outstanding properties of polytetrafluoroethylene with the requirements of processes such as extrusion and injection moulding technology. These fluoroplastics are therefore also suitable for the manufacture of extruded films.

2 Physical characteristics

2.1 Typical materials

In film applications the following fluorothermoplastics are most commonly used: ETFE, FEP, PFA, PVF, PVDF, and THV. The basic physical data of fluorothermoplastics are summarised in **table 1**. This overview also gives an initial classification of the material performance in comparison with polyolefins and PVC.

Here is an outline of the characteristics of fluorothermoplastics that are particularly useful in architectural designs and outdoor applications.

ETFE (ethylene-tetrafluoroethylene) is a partially fluorinated copolymer that is occasionally modified by a third monomer to attain certain properties. The melting point ranges from 220 to 280 °C. ETFE is very transparent (transmission > 90 %), but can also be dyed if necessary, using pigments. Due to its high chemical resistance, ETFE withstands many aggressive media including cleaning chemicals, bird droppings and acid rain.

FEP (tetrafluoroethylene hexafluoropropylene copolymer) is comparatively soft, chemically inert and, like PTFE, characterised by good sliding properties. The main field of application for FEP is wire and cable insulation, but it is also used in films and adhesive tapes. It is characterised by an outstanding UV and visible light transmission. The refractive index of FEP is the lowest of all fluorothermoplastics, approximately corresponding to that of water.



Fig. 1: The sun protection sails covering the Café Mozart in Vienna, Austria, are made from a yellowing-resistant, translucent PTFE fabric.

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PFA, copolymers of tetrafluoroethylene and perfluoroalkoxyvinylethers, are closest to PTFE with regard to its physical and chemical properties but are suitable for injection moulding and screw extrusion. PFA can withstand temperatures of up to 260 °C – the highest continuous use temperature in all fluorothermoplastic materials. Due to this PFA is an alternative to FEP where exposure to particularly high temperatures is required.

PVDF (polyvinylidene fluoride), either as a homopolymer or as a copolymer with hexafluoropropylene or chlorotrifluoroethylene, can be processed at lower temperatures than other fluoropolymers due to its lower melting point (between 135 and 175 °C, depend-

ing on the composition). Nevertheless, it is characterised by high mechanical strength and dimensional stability, good chemical resistance and low permeation rates. PVDF is therefore popular for use in applications such as surface finishing or surface protection, for instance for the refinement of PVC surfaces. It is also used in anti graffiti films.

THV (a polymer composed of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride) can also be processed at low temperatures. THV has an outstanding flexibility and transparency, but can also be bonded to elastomers and polyolefins. These properties make it ideal for use in multilayer films. UV-resistant films made from 3M Dyneon THV are also suitable for the sealing of fabric laminates.

2.2 General properties

As **table 1** shows, these members of the fluorothermoplastic polymer family stand out from "classic" thermoplastic film materials due to their ability to withstand higher continuous use temperatures and because they have a higher fire classification. This resistance to high temperatures covers the full range that plastics must withstand in outdoor applications – including areas in which heavy sunlight and a considerable accumulation of heat is to be expected. At the lower end of the temperature scale, several fluorothermoplastics are able to remain elastic even in conditions where other plastics tend to become brittle.

PTFE, PFA and FEP are characterised by a largely universal resistance to acids, bases and organic solvents that goes beyond that of polyolefins and PVC. ETFE is only sensitive to some ketones, amines and furans, although greater attention must be paid to the nature of the media that comes into contact with PVDF and THV. However, these materials are also resistant to most inorganic and organic acids, alcohols and other hydrocarbons.

2.3 Important properties for film applications

2.3.1 Mechanical properties

A key factor for film applications is the high tear propagation resistance of fluorothermoplastics (**fig. 2**). ETFE, in particular, achieves outstanding values here, making these films ideally suited for all applications where mechanical robustness is required. THV, for instance, reaches the level of BOPET (biaxially oriented PET); the characteristic values of the other fluorothermoplastics are at a similar order of magnitude.

Table 2 summarises some characteristic values of fluorothermoplastic films commonly available on the market. Naturally these characteristic values cannot be transferred entirely: Taking PTFE as an example, **table 3** shows the influence that the film manufacturing process has on the material properties of the films. Available film widths and film thicknesses vary greatly, while the

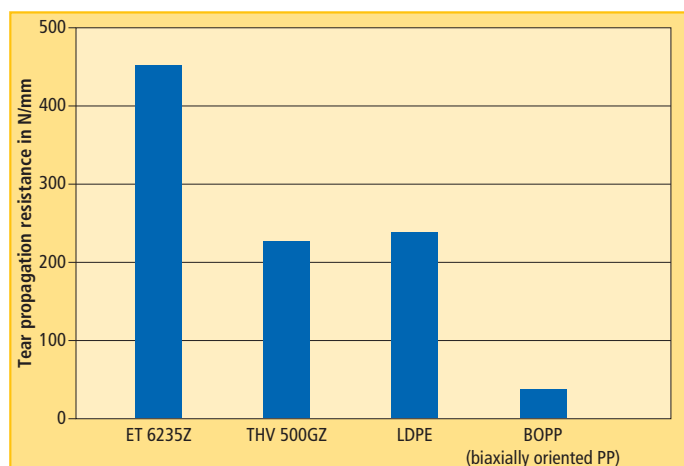


Fig. 2: Tear propagation resistance of ETFE (3M Dyneon Fluoroplastic ET 6235Z) compared with other films (measurement according to DIN 53363)

Tab. 1: Physical data of selected thermoplastics (source: Dyneon)

	PVDF	PVDF flex	ETFE	PTFE	PP	HDPE	PVC
Density (DIN 53497, g/cm ³)	1.78	1.78	1.7–1.76	2.12	0.90–0.92	0.95	1.42
Tensile strength (DIN 53455, N/mm ²)	30–50	28–41	40–46	20–40	33	24–29	45–55
Elongation at break (DIN 53455, %)	20–60	300–400	200	140–500	20–800	100–1 000	20–30
Upper continuous use temperature (°C)	150	120	150	260	100	85	60
Lower continuous use temperature (°C)	–40	–30	–190	–200	–15	–50	–15
Melting point (DIN 53736, °C)	172–178	155–160	270	– / (330)	165	130	160
Fire class (UL 94)	V-0	V-0	V-0	V-0	HB/V-2	V-2	V-0

Tab. 2: Properties of fluorothermoplastic films (source: Dyneon)

	ETFE	FEP	PFA	PVF	PVDF	THV
Film thickness (µm)	12–300	12–500	12–750	12–50	12–500	12–250
Film width (m)	<2	<2	<1.5	–	<2	<2
Tensile strength (MPa)	40–55	25–30	15–25	30–40	35–50	25–30
Elongation at break (%)	300–500	300–350	300–400	100–200	20–200	300–500
Modulus of elasticity (MPa)	900–1 100	500–600	500–600	–	2 200–2 500	200–300
Continuous use temperature (°C)	150	205	250	105	130	130
Chemical resistance	++	+++	+++	+	+	+

continuous use temperatures and the chemical resistance are inherent to the polymer and thus stay pretty much the same. Tensile strength and elongation at break are also subject to certain variations, depending on the production process. This must be taken into account during use.

Many fluorothermoplastics and the films made from them can maintain this extremely high property profile in tensile tests over a wide temperature range. Although the tensile strength of ETFE, FEP and PFA decreases between room temperature and 200 °C, the elongation at break of PFA and FEP films generally remains constant. In the case of ETFE, it even increases considerably up to +140 °C.

2.3.2 Self-cleaning properties

Films made of fluoroplastics also benefit from their self-cleaning and dirt repellent properties. The surface tensions of the polymer materials decrease in the order PA>PET>PEEK>PE>PVDF>ETFE>PTFE. This means that rain water rolls off the surface of the fluoropolymer and takes loose dirt with it (fig. 3). This effect can also be correlated with the contact angle that polar liquids, such as water, form with the surface of a fluorothermoplastic; from angles of contact of around 90° upwards they are considered to be hydrophobic. Water forms a contact angle with PTFE of well over 100°; as the number of C-H bonds in the polymer increases, however, the contact angle reduces slightly (due to the increasing polarity of the polymer) [2].

2.3.3 Resistance to heat and weatherability

In a long-term test, the Swiss Federal Office of Energy determined that films made of FEP and PVF achieved the same or even better light and UV transmission values after 20 years of open air exposure and cleaning with ethanol as compared to new films. Deterioration of the transparency due to material degradation can therefore be neglected. Conversely, in the case of samples made of PC, PET, PVC and unsaturated polyester, significant degradation effects were recorded in the same test (these included discolou-

ration/yellowness, formation of mould and embrittlement) [3].

The film's high resistance to mechanical influences also became apparent in long-term tests: None of the fluoropolymer films examined, which were only 25 to 120 µm thick, showed any significant damage after 20 years of open air exposure at two different locations in Switzerland.

Fluoroplastics still looked good after long term exposure to even more demanding conditions. In ageing tests carried out by Dyneon, ETFE showed no detectable visual impairment after 10,000 hours of exposure to UV irradiation (xenon test 150) and with regard to their mechanical characteristics, the samples tested lost less than 10 % of their performance. Very similar results were recorded after seven years, ten years and 20 years of open air weathering in Bombay, Arizona and Southern Germany. Experts concluded from this that ETFE roof constructions offer a lifetime twice than of those made of PVC.

A detailed assessment of the weathering or ageing properties of fluorothermoplastics, as well as the dependence of their mechanical properties on temperature can be found in [4].

3 Film manufacturing processes

Films made of fluorothermoplastics are usually manufactured by means of extrusion, using either the blown film method or the flat film method with a slot die. The correct cooling procedure is essential here in order to achieve the desired properties

making the chill roll assembly a most crucial part of the equipment [5]. In the flat film method, film thicknesses of 10 to 300 µm are possible, in special cases up to 500 µm. Typically these films are up to two metres wide.

In the blown film method, films are also manufactured with a width of up to two metres but thicknesses range typically below 150 µm. The main reason for this is the high density of the fluoropolymers. Due to this, thicker films simply can't support their own weight during the blowing step. THV or ETFE films with a thickness of just 100 µm have a weight per unit area of around 200 or 175 g/m² respectively. To operate a typically high throughput blown film extrusion line is an economic challenge, too due to the comparatively high raw material prices

Fig. 3: The inner courtyard of the William Rappard Centre of the World Trade Organisation in Geneva, Switzerland, is spanned by Nowoflon ET 6235Z films made from ETFE. Plants and trees can grow under this self-cleaning, transparent construction. (Copyright: WTO)



Tab. 3: Properties of PTFE films (source: 3M / Dyneon)

	S-PTFE skived	E-PTFE extruded, sintered	E-PTFE extruded, unsintered	E-PTFE dispersion cast
Film thickness (µm)	12–300	50–250	50–250	12–125
Film width (m)	<1.5	<0.2	<0.2	<0.15
Tensile strength (MPa)	20–30	40–50	5–12	25–30
Elongation at break (%)	200–300	150–300	50–100	400–500
Modulus of elasticity (MPa)	600–650	600–650	600–650	600–650
Continuous use temperature (°C)	260	260	260	260
Chemical resistance	+++	+++	+++	+++

of the fluoropolymers. Therefore, and also because of the superior caliper uniformity, flat film extrusion is the preferred method for producing fluorothermoplastic films.

Alternative technologies have to be used to manufacture PTFE films. Granular PTFE (S-PTFE, suspension PTFE), for instance, is pressed into a mould under a pressure of 150 to 350 bar and sintered at temperatures of around 370 °C [6]. The semi-finished materials manufactured in this way are characterised by a homogeneous structure. Films with various thicknesses can be produced from such blocks using the skiving method. The machines used for this are reminiscent of lathes and the process is similar to making wooden veneers.

E-PTFE, polytetrafluoroethylene produced in the form of a fine powder by the emulsion process, can be processed into films by means of paste extrusion and calendaring. The powder is mixed with a hydrocarbon lubricant and initially pressed at about 10 to 50 bar into a cylindrical preform. This so called "green body" is then pressed through a shaping die. Finally, the extrudate is calendared between two rollers to form the film. Several steps may be required for this depending on the thickness of the film. After this, drying takes place by exposing the film to temperatures of between 160 and 200 °C until the lubricant has evaporated. In some cases, additional sintering may be required. Films manufactured in this way can also be stretched to achieve particular characteristics.

Films can also be made by coating or spraying aqueous dispersions of this polymer

onto rollers, belts or precursors. The coating is then dried and peeled off; the resulting film may also be sintered. This method is suitable for the manufacturing of multilayer films, but is fairly expensive [7, 8].

4 Choosing the right fluoropolymer films for the right applications

Films made of fluoropolymers are used in a wide range of industrial applications. These range from release films (e. g. in electronics or composite manufacturing) to adhesive tapes to pharmaceutical packaging and all the way to architecture and solar technology. This article focuses on fluorothermoplastics in outdoor applications.

4.1 Solar industry

Fluoropolymer films can increase the efficiency, reliability and profitability of photovoltaic systems. Thin films made of fluorinated polymers can exhibit a solar transmission coefficient of more than 0.9, which even exceeds that of iron-free glass [3]. The high light transmittance achieved using fluoropolymer films is coupled with outstanding resistance to UV rays, moisture and weathering – the factors that strongly limit the lifetime of conventional solar module components.

As a result, thin ETFE films, such as Ultra Barrier Solarfilm 9L from 3M, can successfully replace the protective glazing of solar panels. Fluorothermoplastic films are often used in solar technology in the form of multilayer film constructions. An exam-

ple of this is backsheet films in which a THV surface layer is combined with a puncture-proof PET intermediate layer and an EVA adhesion layer to create a firm connection with the solar modules. This construction is also characterised by outstanding electrical insulation properties (partial discharge voltage > 1,100 VDC). The great technical challenge in the production of these films is ensuring a good bond between the fluoropolymer component and the other layers. 3M has gained a high degree of expertise in this field over the past decade and has sold films with THV layers of various thicknesses under the Scotchshield brand since 2006. These conform to the UL 1703, IEC 61215 ed. 2 and IEC 61730 standards and are used worldwide by solar module manufacturers.

Fluoropolymer films can be used as an alternative to glass and offer a range of benefits, including weight reduction which facilitates assembly and reduces the cost of logistics. Due to their high flexibility, the films are also more tolerant of assembly errors. Overall, fluoropolymer films can contribute to a reduction in the cost of solar modules and help secure long term investment in this kind of equipment.

4.2 Construction and architecture

Plastics are relatively young materials in the building industry and were used for the first time in the 1940s. Films made of fluorothermoplastics are now revolutionising the industry and have opened up a range of aesthetically pleasing possibilities for architects across a range of applications. Typically films with thicknesses of 50 to 300 µm are used which are characterised by a comparatively

Fig. 4: The entrance to the Federal Chancellor's Office in Berlin, Germany, is probably one of the most photographed fluoroplastics applications. The construction consists of a PTFE-coated glass fibre fabric.



Fig. 5: Sports stadia – here the Manaus Stadium in Brazil shows a popular application for fluorothermoplastic films. (Copyright: M. Bredt)



low weight per unit area. Fluoropolymer films can be easily joined together by contact welding. Due to their extreme longevity they are fully recyclable and will thus have no adverse ecological influence.

Fluorothermoplastics are not the only polymer materials used in the building sector. Polycarbonates (PC), PMMA, stabilised polyolefins (with restrictions) and polyesters are also often used, although these polymer materials are not seen as direct competition for fluorothermoplastics.

That is due to the superior weatherability of fluorothermoplastics as well as their suitability for use in aesthetically pleasing architectural features for building projects. Fluoroplastics are mainly used in two special fields of application: firstly as a coating material in the "textile architecture", where the origins of the design lie in tent construction (fig. 4 and 5) and secondly in transparent or translucent ETFE film constructions, for example in the form of roof and wall structures made from segmented air cushions. In both cases the webs must be supported by metal frame or rope structures. ETFE offers several advantages over glass in this application, including having a strong resistance to hail and breakage as well as being lighter. Glazing used in architecture is also very strong, but due to its weight it requires considerably heavier substructures than films.

The decision of whether to use fluorothermoplastic film or a fluoropolymer-coated fabric generally comes down to a question of whether the client wants a transparent,

glass like design or a classic tent construction. This can be illustrated by the following example. If a new indoor swimming pool is to be built as cost effectively as possible, an inexpensive sheet metal roof will probably be chosen. If, on the other hand, numerous paying visitors are to be attracted, for instance to a leisure park, an ambitious design with transparent elements or an opaque tent roof can make economic sense (fig. 6). If a transparent solution is chosen, the question is then whether this should be executed in glass or a similar plate material (e. g. PMMA), or if, in fact, a more futuristic, aesthetically appealing design is called for, then fluorothermoplastic films come into play.

If a transparent solution can be used at all, is many times also a question of mechanics. In cases where large distances need to be spanned, such as for a sports stadium with a wide grandstand, an opaque fluoropolymer-coated fabric, such as glass fibre fabric with PTFE coating, offers a good option. This solution, which was successfully used for the Olympic Stadium in Berlin, demonstrates that fabric and film solutions do not

have to compete against each other for large projects, but can, in fact, complement each other.

As outlined in the introductory section, the most important fluorothermoplastic used for films in architectural applications is ETFE. Although FEP and PFA can also offer a number of positive characteristics, the sum of its properties makes ETFE the material of choice for this area of application. Apart from its transparency, the high temperature resistance of ETFE and the excellent mechanical properties over the entire application temperature range are the key factors used in the decision making process. The distinguishing properties are the tensile stress at 10 % elongation and the tear propagation resistance.

THV films have recently been used in architectural applications, particularly in the form of fabric reinforced laminates. PVDF as a film is rarely used by architects due to its lack of transparency, although it is sometimes used in fabric applications for interior decoration projects.

Fig. 6: Lightweight, attractive roof structures made from ETFE films can help to make structures particularly appealing to guests. This example shows the Prienera swimming pool in Prien, Chiemsee, Germany.



Fig. 7: The façade of the mountain station of the glacier cable car on the Gaislachkogel, Austria. ETFE films (Nowoflon ET 6235Z) are used and have been designed to withstand extreme wind loads, high UV levels and low temperatures. (Copyright: A. Niederstrasser)



Fig. 8: The "biomes" at the Eden Project in Cornwall, UK, consist of a cushion construction made using ETFE. Films made from Dyneon ETFE let pass 90 % of the visible light and 80 % of the UV-A light.



4.3 Application examples

The capabilities of modern fluorothermoplastic films in architectural structures can be illustrated using three examples.

4.3.1 The mountain station of the glacier cable car on the Gaislachkogel, Austria

On the Gaislachkogel in the Austrian Alps, at an altitude of more than 3,000 m, stands the highest situated polymer-film structure in the world: the terminus of the cable car (fig. 7). Here, the structure not only has to withstand high wind loads, but also temperatures as low as minus 60 °C. The film, made from 3M Dyneon Fluoroplastic ETFE, was chosen for its extraordinary tensile strength as well as its resistance to low temperatures and UV radiation. In addition, the low surface energy not only reduces gradual soiling, but also avoids snow build-up on the structure.

4.3.2 The inner courtyard of the WTO headquarters in Geneva, Switzerland

By contrast, the significantly lower weight of ETFE compared with glass was one of the reasons why the inner courtyard at the headquarters of the World Trade Organisation in Geneva was spanned by ETFE cushions (fig. 3). A total of 105 elements made from air-filled ETFE films (Nowoflon ET 6235Z made of 3M Dyneon ETFE) are approximately 95 % lighter than an equivalent glass construction. This made a simpler support structure possible that emphasises the open, light

character of the roof. Thanks to the high UV transmittance of the ethylene tetrafluoroethylene copolymer, vegetation including trees can grow under the roof. The low soiling tendency of the material also largely eliminates the need for manual cleaning. The film manufacturer Nowoflon has been using fluoropolymers from Dyneon for 30 years, providing additional reassurance.

4.3.3 The Eden Project in Cornwall, United Kingdom

The Eden Project in Cornwall, southwest England, is one of the most iconic structures in the world and wouldn't have been feasible without the use of fluorothermoplastic films. The series of biomes, domes or spherical structures made from transparent ETFE film, are a major tourist attraction of the area (fig. 8). The design is inspired by the geodesic domes of the American visionary and architect Richard Buckminster Fuller. The biomes consist of hundreds of hexagonal and pentagonal cushions made of ETFE film supported by a lightweight steel structure. As well as being lightweight, ETFE cushions are also characterised by good thermal insulation properties. The U-values of multilayer ETFE cushion structures lie in the range of 1.2–2 W/m²K, creating an ideal greenhouse climate under the domes.

5 Solar heat management

The accumulation of heat under sun lighted roof areas made of fluorothermoplastic films can create a challenge for architects. ETFE films are largely transparent to visible

light and to wavelengths from the near-infrared range (NIR) (fig. 9). That means that people walking under the roof are fully exposed to the radiant heat of the sun.

In order to prevent this, steps can be taken to avoid or reduce direct exposure to sunlight – for example by printing patterns on the film, dyeing the film (usually white) or by attaching mechanical shading devices, such as louvers, to weaken the transparency of the ETFE films.

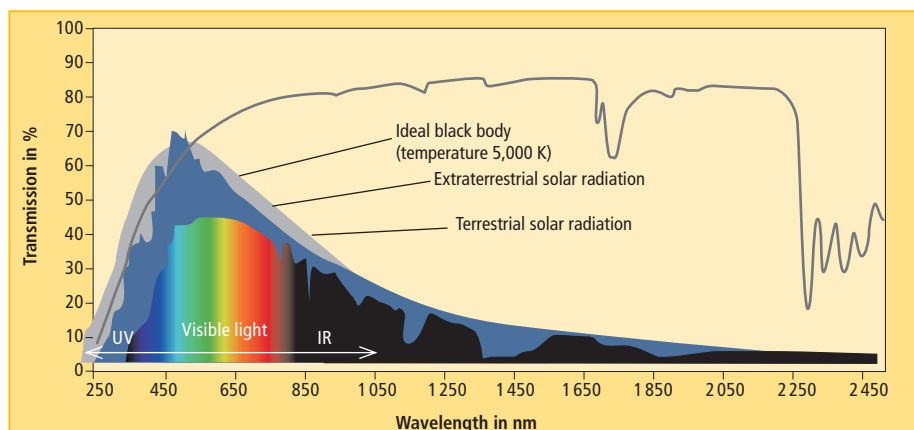
However, a far more innovative solution is to change the physical properties of the film so that visible light is let through, but not the high energy infrared component of sunlight.

This could be achieved by incorporating optically transparent pigments that reflect light in the near infrared range, but a more flexible solution is offered by using multilayer optical films (MOFs). These have been available since the end of the 1960s and have undergone a rapid development since around 1990. These films work by using the effect of light reflected at the phase boundaries of materials with different optical densities. By intelligently varying the layer thicknesses and refraction indices, it can be influenced which wavelength range of the light will be reflected. By using special layer structures, MOFs can be created that block the radiation in a very sharply defined wavelength range.

Polymer materials are ideal for the manufacture of MOFs in order to purposefully control the reflection properties of these films. The key parameters are refractive indices, the number of layers, layer thickness and the materials themselves. Commercially available MOFs consist of many hundreds of individual polymer layers, which results in extremely sharply defined reflection bands. This technology is far beyond what's typically known as classic coextrusion.

As an example of technical performance, one type of MOF can reflect the spectral range of sunlight between approximately 870 and 1,100 nm (fig. 10). Another product can block an even broader wavelength range of between approximately 700 and 1,300 nm and therewith a spectral region

Fig. 9: The transmission of ETFE films in comparison with the spectrum of sunlight



in which the sun emits a major part of its perceptible infrared radiation to the earth's surface (fig. 11). These films could then be incorporated in designs such as ETFE cushion constructions.

New MOF film developments combine the advantages of fluorothermoplastics with multilayer technology: Not only will they prevent the accumulation of heat by the reflection of specific radiation portions of the sunlight, while almost fully retaining transparency in the visible range of the spectrum, but they will also exhibit weathering properties similar to classic ETFE films.

As the products are made exclusively of polymer materials and contain no metals, these multilayer films don't create a barrier to mobile telephone signals, unlike metal-coated thermally insulating glazing solutions. Infrared impermeable MOFs can also be combined with other fluorothermoplastics to create an endless range of possibilities for architects to explore and develop applications using these versatile materials even further.

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Fig. 10: With the aid of refractive effects, multilayer optical films (MOFs) can filter out certain ranges of the electromagnetic spectrum.

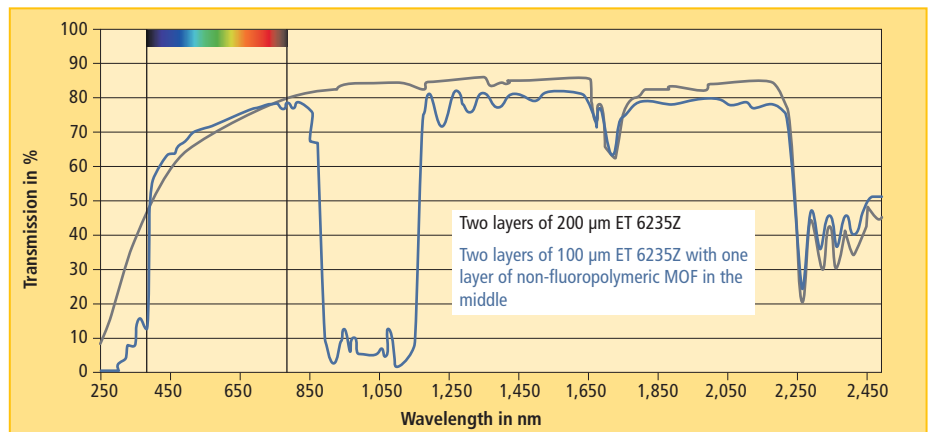


Fig. 11: Multilayer optical films can reflect infrared radiation without affecting transmittance for visible light. As a result, the excessive accumulation of heat under the film is eliminated and thanks to two ETFE surface layers, the construction is also resistant to weathering.

