MBS - Specialty Plastic Films 2001
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KYNAR® FILMS

NOVEL PVDF MULTILAYER BLOWN FILMS

Abstract

The properties & applications of a new family of multilayer PVDF Film are presented hereafter. KYNAR® Films combine the outstanding properties of Fluoropolymers - UV Insensitivity, Chemical & Fire Resistance, Low Surface Tension - with the flexibility of the blown extrusion process – one step production of wide multilayer films with build in adhesive layer. PVDF Films can be laminated directly onto various thermoplastic, thermoset or primed metal substrates and will durably protects the aesthetics of UV sensitive substrates.

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A) Introduction : Market Requirements for Durable Aesthetics

A-1) Necessary Features of a Durable Film

Prospective users of specialty films for exterior applications sum up their needs under one simple requirement : durable protection of the aesthetics of their parts. Obviously the film should also be easy to handle, easy to apply to the substrate and cost effective. More precisely the film must have the following primary features :

1. UV Stability — Color & Gloss Retention, No Fading / Chalking
2. UV Opacity — UV Protection of the Substrate Underneath
3. Chemical Resistance — Surface Integrity & Ease of Cleaning
4. Mechanical Property — Film Handling & Multilayer Part Impact Resistance
5. Adhesion — Durable Bonding

The following secondary features are also highly desirable :

1. Low Surface Tension — Low Dirt Pick Up, Low Soiling
2. Barrier Properties — Moisture Protection
3. Surface Hardness — Scratch Resistance
4. Fire Retardancy — Safety

A-2) Chemical Resistance & Anti Graffiti

Chemical resistance is becoming more and more important because of the enduring problem of graffiti removal. As truly self cleaning surfaces are not yet available, an all around high chemical resistance (and good barrier property to the chemicals used) is necessary to ensure that graffiti can be easily removed using increasingly potent stain removers without leaving a ghost on the substrate.

A-3) UV Opacity in Transparent & Pigmented Film

The lasting appeareance of the finished part over the desired lifetime means that the protective films must maintain UV opacity as long as possible. As will be discussed hereafter, this is more of a challenge in a transparent film – where organic UV absorbers[1] are used – than in a pigmented film - where mineral UV absorbers are used.

A-4) An Emerging Trend : Decoration & Customization

The ability of the film to be further printed & decorated is an important feature in creative applications such as automotive because it allows the customization of finisihed parts. This requires transparent films with durable UV opacity to protect the print.

[1] Such as Benzophenone, Benzotriazole or Triazine

B) Specialty Films Offering Durable Protection : Acrylics & Fluoropolymers

As one can see « durable aesthetics » - often referred to as weatherability - really entails a complex combination of physical properties which become more difficult to assemble as protection expectancy increases. Indeed, once talking in terms of years for automotive (5 to 10 years) or building (7 to 30 years) application, the choice for a film able to meet these requirements quickly narrows down to 2 families : Acrylics & Fluoropolymers. While possessing good property profiles, other known polymer families (polyolefines, polycarbonates, polyurethanes, polyamides, polyvinylchlorides, polyesters) simply fail prematurely because of insufficient UV stability of the polymer matrix.

B-1) Acrylics : Impact Modified Polymethylmethacrylate (IM-PMMA)

Protective films described as Acrylics are generally prepared from a blend of PMMA and impact modifier because PMMA alone is fairly rigid (Elastic Flexural Modulus (E) ~ 3500 – 4000 MPa) and thus quite brittle. As such it would not make a useful film because it would be difficult to handle and would embrittle the substrate upon multiaxial impact. Moreover obtaining good and lasting adhesion - even on compatible substrates such as Acrylonitrile/Butadiene/Styrene (ABS) – would also be difficult: a crack would propagate easily at the interface once initiated (think of a rigid microscope glass slide on a flexible substrate). Thus PMMA is generally formulated (up to 50% by volume) with core shell impact modifier.

To maintain the good UV resistance of pure PMMA, the constitutive monomers of the core shell impact modifier are also acrylic in nature. The diameter of the core shell particle is kept small (< 250 nm) and its refractive index is adjusted to match that of the resin and maintain the optical clarity of the film. In such blends E can be below 2000 MPa. If a copolymer of MMA and another, lower glass transition temperature (Tg) monomer (such as Ethyl Acrylate or Butyl Acrylate), is used as the polymer matrix, even more flexible films can be obtained (E < 1000 MPa). These films are manufactured by cast film extrusion or blown film extrusion and are available commercialy from several sources. Acrylics Films offer the following balance of advantages / limitations :

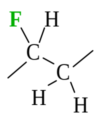
ADVANTAGES	LIMITATIONS
1. Excellent Aesthetics (Highly Transparent, Low Gloss, Printable) 2. Good Adhesion to a Variety of Substrate 3. Good Formability 4. Lower Cost	1. Fading & Chalking under Long Term UV Exposure 2. Insufficient Solvent Resistance & Cleanability 3. Low Barrier Properties 4. Low Tear Resistance

The limitations are mostly due to the fact that the core shell impact modifiers present in acrylic films are not as UV resistant as PMMA and that they can be easily swollen by organic solvents.

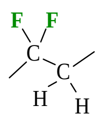
B-2) Fluoropolymers: Polyvinylfluoride (PVF) & Polyvinylidenefluoride (PVDF)

Fluoropolymers are known for their excellent stability when exposed to harsh thermal, chemical, and ultraviolet environments. This rare combination is due to the strenght of the C-F Bond, one of the most stable bond known in organic chemistry (Bond Dissociation Energy : C-F = 136 kcal/mol ; C-H = 81 kcal/mol). The fluoropolymer family is made up of several partially of fully fluorinated homopolymers and copolymers :

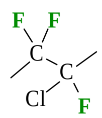
Homopolymers



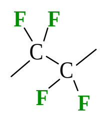
Polyvinyle fluoride
PVF



Polyvinylidene fluoride
PVDF

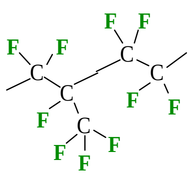


Polychloro-trifluoroethylene
PCTFE

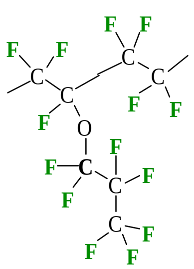


Polytetrafluoro-ethylene
PTFE

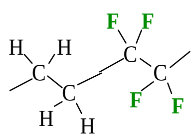
Copolymers



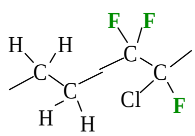
Tetrafluoroethylene + perfluoropropene
FEP



Tetrafluoroethylene + perfluoropropylether
PFA



Tetrafluoroethylene + ethylene
ETFE

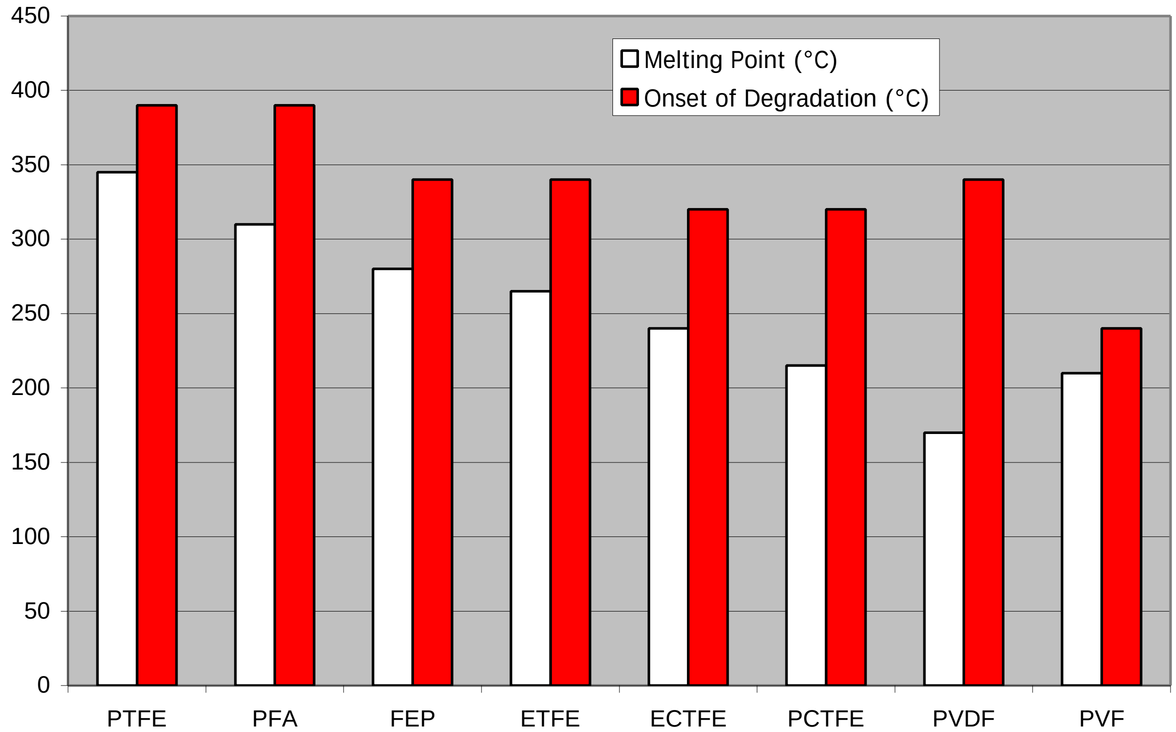


Chlorotrifluoroethylene +ethylene
E-CTFE

As high performance specialty films, mainly PVDF & PVF are encountered on the market place with two different situations :

	PVDF	PVF
F Content (wt. %)	59	41
Melt Processible	Yes	No
Resin Producer	4	1
Film Producers	> 4	1
Available Processing Technology	Solvant Cast, Blown Film Extrusion, Cast Film Extrusion	Oriented Extrusion From Gel

PVF is produced by DUPONT under the tradename TEDLAR® and is available almost exclusively as films. By contrast, there are 4 main producers of PVDF granules among which ATOFINA is the global leader in terms of capacity under the KYNAR® tradename. PVDF films are produced by a variety of manufacturers (resin producers & independent converters) and processes (Solvant Casting, Blown Film Extrusion, Cast Film Extrusion, Biorientation). PVF films are manufactured by a process similar to oriented gel extrusion. The difference in film production is due to the fact that PVDF is one of the only melt processible fluoropolymers thanks to a wide processing window :



Both PVDF & PVF have been available for almost 40 years as superior protective coatings and have gained large market acceptance. As a solvant based dispersion coating, PVDF has been applied – under the Tradename KYNAR® 500 – for over 35 years to various metallic substrates and has demonstrated outstanding weatherability in terms of Color Stability & Gloss Retention. Millions of m2 are coated yearly with PVDF Paints supplied by Coil and Spray Coaters to the construction industry. However, in the paint process, solvent removal is done by burning which in turn fuels the coil coating furnaces but limits the process to metallic substrates. Thus, in the late 70's ATOFINA pionereed and developed the co-extrusion of PVDF onto various thermoplastic substrates (PVC, ABS, PC, Polyolefines) which lacked weatherability. This technology allows the production of weatherable sheets which can be further thermoformed. The development of free standing PVDF films is thus the next genearation in the evolution of PVDF use in new applications :

KYNAR® Multilayer Blown Films &

Corresponding Coextruded Thermoformed Panels (PVC Substrates)

C) KYNAR® Blown Films : A Innovative Combination of High Performance Polymers & Multilayer Technology

C-1) General Overview : The development of KYNAR® Films was conducted with 3 guiding thoughts in mind :

① Optimum Material Selection for High Film Performances,
Flexible Production Process and
Operationnal & Cost Efficiency

MATERIAL SELECTION : The thermodynamic miscibility of PVDF and PMMA was taken advantage of in several ways. First, highly weatherable and transparent clear coats with excellent chemical resistance can be obtained from blends of PVDF homopolymer with a low fraction of PMMA[2]. Second, patented compositions of PVDF, PMMA and weatherable core shell impact modifiers open the way for tough, flexible adhesive compositions – known as ADHEFLON® - which act as thermoplastic tie layers onto various thermoplastic, thermoset or primed metal substrates. Third, PMMA is used for more efficient mixing & distribution of the various additives (UV absorbers, mineral pigments, fire retardant fillers, …) used in the films ; this point is essential as fluoropolymers are not known to accept easily (or without danger) large quantities of additives. Last but not least, PMMA allows to decrease the cost of fluorinated resin film without compromising the property balance.

FLEXIBLE PRODUCTION : The patented multilayer blown technology allows the production of films without residual solvent or plasticizer ; furthermore, the films can be both :

a) thin or thick – typically from 10 to 100 µm ; this is an advantage over solvant casting or gel extrusion, because higher film gauge does not necessarily means lower productivity; however solvant casting allows the production of film with low gel content.

b) narrow or wide films – typically from 1200 up to 1800 mm depending on film formulation & thickness; blown extrusion allows the production of wider films than cast extrusion because of less limitations in terms of die size.

OPERATIONNAL & COST EFFICIENCY : while there is generally no questions about their technical performances, economic efficiency is a must for fluoropolymers films if they are to be further developed. We believe KYNAR® film can be offered competitively because ATOFINA is integrated in the production of both PVDF and PMMA (powder &

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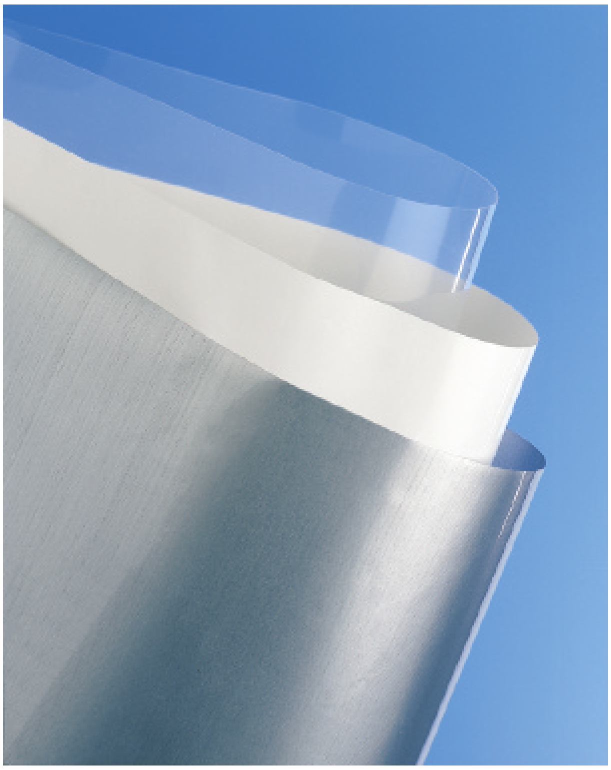
2 as a semi crystalline engineering resin, PVDF homopolymer alone is hazy even at low thickness

granules) and because blown film extrusion is a highly productive process. Moreover the multilayer approach allows greater integration – a source of cost savings - into one single film of various properties (Surface Gloss & Chemical Resistance, UV opacity, Mechanical Properties, Adhesion); an example of such integration is given in the schematic hereafter, where each layer is typically 10 to 20 µm thick :

KYNAR® Clear Coat for Gloss, Chemical Resistance & Zero Metal Marking
KYNAR® Layer, Iridescent or Metallic Effect for Aesthetics
KYNAR® Layer, Base Color for UV Protection of the Substrate
ADHEFLON ® Thermoplastic Adhesive for Adhesion & Impact Resistance

Note that the adhesive is build in the film and need not be applied in a separate step.

C-2) Product Range & Processing Guidelines : The starting product range includes both mass-tinted and transparent films (30 or 50 µm thick) which can be printed with a variety of designs :



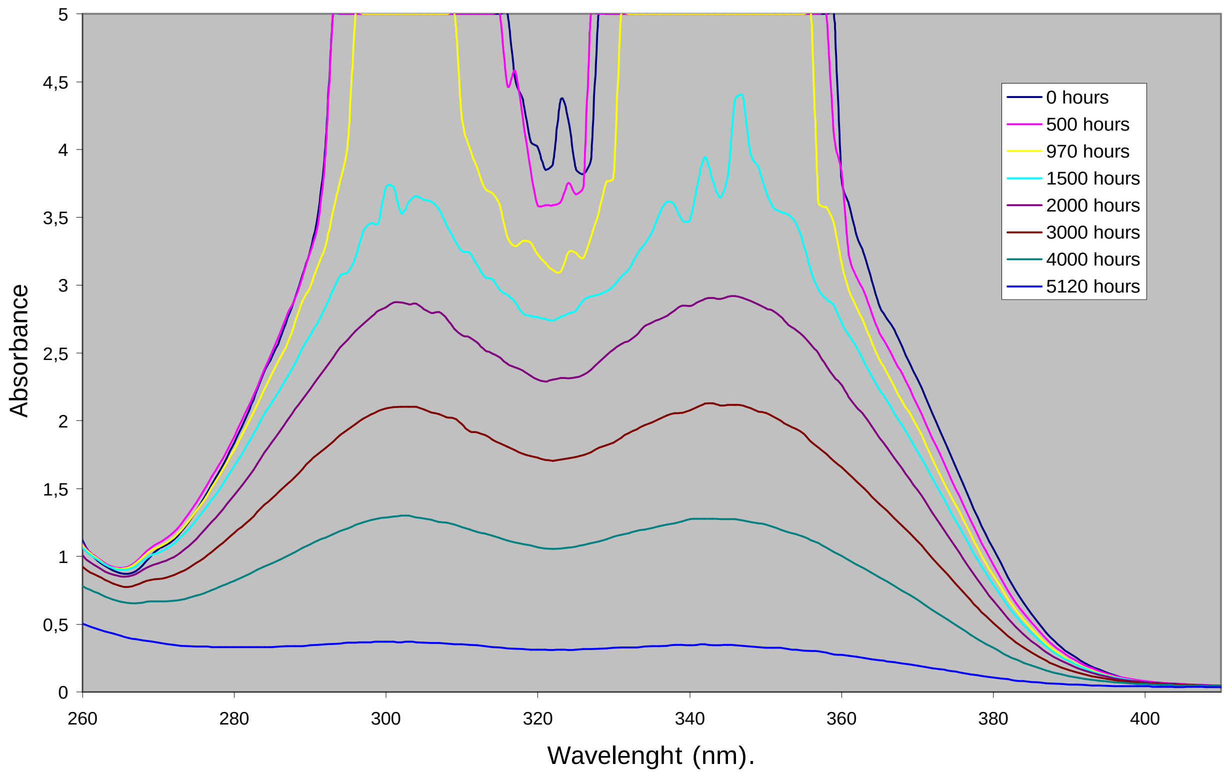
The films are generally applied by heat lamination (typically from 130 to 240°C) to the substrate (see KYNAR® Film General Brochure for the complete Grade Description & Application Guide).

C-3) Properties of Transparent & Pigmented Films : The table hereafter summarizes typical properties of a Transparent and White PVDF Film :

	Test Method	Units	White Film	Transparent Film
Structure	-		Monolayer	Bilayer
Thickness	ISO 4591	µm	50	50
Specific Gravity	ISO 11183	-	1,7	1,4
Unit Weight	-	g/m2	85	70
Area Factor	-	m2/kg	11,8	14,3
Shrinkage at 140°C	ISO 11505	%	-1,5	-1
Moisture Absorption	ATOFINA	%	< 0,2	< 0,3
Transmittance at 560 nm	ASTM D1044	%	NA	95%
Total Haze	ASTM D1003	%	NA	< 5
Dielectric Breakdown Voltage	ASTM D149	KV/mm	200	100
Limiting Oxygen Index (LOI)	ISO 4589-2	%	38	20
Elastic Tensile Modulus	ISO 1184 = ASTM D882-95A (50 mm/min)	MPa	1900	1400
Stress at Yield		MPa	30	20 - 25
Strain at Yield		%	3,5	4,0
Elongation at Break (Machine Direction)		%	> 150	> 150
Elongation at Break (Transverse Direction)		%	> 150	> 100
Stress at Break (Machine Direction)		MPa	35	30
Stress at Break (Transverse Direction)		MPa	35	25
Tear Strength (Machine Direction)	ISO 6383-2 Elmendorf	cN	30	12-14
Tear Strength (Transverse Direction)		cN	40	16-20
Tear Strength (Machine Direction)	ISO 6383-1 Elmendorf	N/mm	14	4
Tear Strength (Transverse Direction)		N/mm	18	4

The above property profile compares favorably with previously mentionned commercial PMMA & PVF films. The excellent mechanical properties of the film mean that it will not break when pulled upon during a lamination step. Most of the properties reported in the above table can be further tailored through specific material selection ; this is especially true of Fire Retardancy, Barrier Properties & Chemical Resistance.

C-4) UV Opacity of Transparent Film : transparent KYNAR® Film were formulated with organic UV absorbers to ① be 99% opaque up to the 400 nm wavelength for at least 2000 hours in the SEPAP[3] 12-24 accelerated weathering test and to maintain a gloss retention greater than 80% and a color shift Delta E lower than 2 after 1000 hours in the WOM[4] accelerated weathering test (a typical requirement in automotive application). The loss of organic UV absorber as the molecules undergo photoxydation is monitored as a function of time :

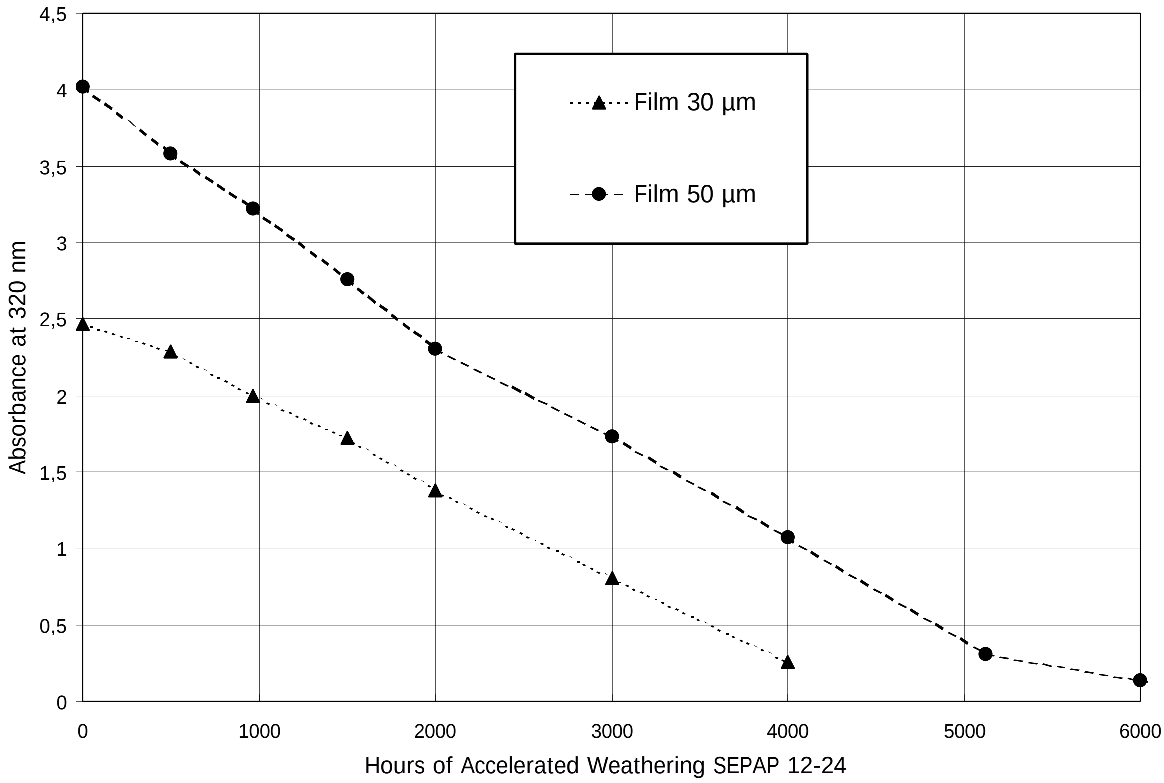


UV absorption spectrum of a transparent UV Opaque PVDF Film in the 260-410 nm region as a function of accelerated weathering time (SEPAP 12-24 test)

[3] SEPAP 12-24 : Climate chamber equiped with 4 artificial lamps (mercury vapor : unit power 400W) with cut off of UV radiation below 300 nm ; samples are continuously exposed without water sprinkling ; temperature is maintained at 60°C

[4] WOM CI135A : Climate chamber equiped with 3 artificial lamps (Xenon arc: 63 W/m2 between 300 and 400 nm) with cut off of UV radiation below 290 nm ; samples are exposed alternatively to the lamps and sprinkled with water for 18 min every 102 min ; relative humidity is maintained at 50% and temperature at 70°C (dry period)

The absorbance at 320 nm (where the dip in the UV absorption spectrum is located) can then be plotted as a function of time to visualize the performance of the film :



Absorbance as a function of accelerated weathering time (SEPAP 12-24 test)

It can be observed that, even in the extremely tough SEPAP test (where exposure to the UV source is continuous), a 50 µm film maintains 99% UV opacity (absorbance of 2) more than 2000 hours and is still 90% UV opaque (absorbance of 1) after 4000 hours.

D) Conclusions : KYNAR® Films, The Durable Protection of Fluoropolymers for Demanding Applications

The overall property profile of KYNAR® Films (Weatherability / Anti Graffiti / Low Dirt Pick Up / Chemical Resistance / Barrier Properties / Fire Resistance / Adhesiveness / Mechanical Strength) make them of great interest as a durable protective films for applications in various fields such as :

1. Construction : Thermoformed Thermoplastics Panels for Facades, Window Profiles, Transparent Roofing Panels, Vinyl Sidings, Thermosets Laminates for Facades or Interiors, Metallic Panels (Aluminium or Steel) for Facade, Vinyl Wall Paper
2. Transportation : Train or Bus Interior, Car & Truck Body Panel, Aircraft Interior
3. Technical Textile : PVC Tarpaulin for Tents, Fire Retardant Textile, Liner for Flexible Tanks, Sails Protection, Protection of Balloons and Blimps
4. Specialty : Photovoltaic, Printed & Decorated Films for Lamination, Protective Labels , Gas Sampling Bags, Chemical Containement, Electrical Tape, etc ...

Meanwhile the multilayer blown film approach is a flexible tool to develop cost effective films closer to market needs. Our R&D team is ready and willling to accompany you in your new developments.

ACKNOWLEDGEMENTS

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