Proceedings of the IASS 2024 Symposium
Redefining the Art of Structural Design
August 26-30, 2024, Zurich Switzerland
Philippe Block, Giulia Boller, Catherine DeWolf,
Jacqueline Pauli, Walter Kaufmann (eds.)

Long-term weathering durability of ETFE membranes with controlled thermal and optical properties

Hiroshi ARUGA, Kouichi ODA

AGC Inc.
10, Goikaigan, Ichihara, Chiba 290-8566, Japan
hirosi.aruga@agc.com

Abstract

We will report the results of a 35-year long-term outdoor exposure test of 60 μm ETFE film in Japan, as well as the actual exposure results and accelerated weathering test results of ETFE film for membrane structures in Japan and overseas. We will discuss the regular transparent, UV protection, and silver printing in detail. 35 years have passed since 60μm transparent ETFE film was first used in outdoor greenhouses in 1988. The breaking strength remained at 93%, and the stress at 10% strain approximately 7% higher than the initial value. The 200μm clear, UV cut, near infrared absorbing, white, and blue printed films have been exposed to Florida for 15 years, and the mechanical properties of each film have hardly changed. However, the UV cut function of UV cut films is gradually decreasing. For single-layer silver printing exposed outdoors, the reflectance has decreased by approximately 23% after 18 years. These phenomena reproduce the results of artificial acceleration tests using carbon arcs and showers. We believe that by reducing the reaction between these heat and light control fillers and ETFE, we will be able to maintain thermal and optical performance longer than these products made over 15 years ago.

Keywords: ETFE, outdoor exposure test, membrane structures, functional film, accelerated weathering test

1. Introduction

1.1 The mechanical and optical characteristics required as ETFE film for membrane structure.

ETFE refers to a copolymer resin of ethylene and tetrafluoroethylene. However, ETFE consisting only of these two monomers is not flexible and transparent, so all ETFE resin manufacturers polymerize a third component and/or a small amount of a fourth component into ETFE. There are a variety of ETFE resins, with melting points ranging from 180°C to 270°C. For membrane structure applications, one with a melting point of 250 to 270°C is used, taking into consideration creep characteristics at 50°C.

The mechanical properties required for ETFE films for membrane structural applications are stress at 10% strain, tear resistance, bending resistance, repeated tensile properties, and creep properties. In addition, from the perspective of thermal and optical properties, ETFE films that adjust UV, visible light, and near-infrared light are required to create a comfortable environment. These performances require durability of 20 years or more.

Such functional ETFE films have already been used in translucent white films (2006 German soccer field), transparent blue films (2008 Beijing swimming pool, China), silver prints (2008 Beijing track and field stadium, China), etc. More than 15 years have passed. However, there are few documents describing their weather durability.

2. Accelerated weathering test and outdoor exposure test

2.1 Weathering test method

There are two types of evaluation methods for accelerated weathering tests: S.W.M. and SUV. The S.W.M is a carbon arc type made by Suga Test Instruments, and the SUV is a metal halide lamp made by Iwasaki Electric.

Figure 1 shows photographs of two weathering accelerated weathering test devices. Figure 2 shows the intensity of the S.W.M, SUV, and Xenon lamps and the intensity of sunlight radiation for each wavelength. S.W.M. has UV radiation characteristics that are very similar to sunlight, so it is a highly reliable accelerated testing device, similar to the Xenon test.

Table 1 shows the operating specifications and UV irradiation amount of each test device. The amount of radiation in the ultraviolet region of S.W.M. is 79W/m^{2,} which is 1.3 times stronger than the 60W/m^2 of sunlight. The intensity of the SUV is 1500W/m^2, which is 25 times stronger than sunlight. The total amount of ultraviolet rays in Florida, USA is 300MJ/m^2 per year. The test time equivalent to 3000MJ/m^2 over 10 years outdoors is 10500 hours for SWM and 660 hours for SUV. When taking a shower, the internal temperature of both devices is approximately 30°C, but the temperature of the black panel (B.P) during light irradiation without a shower is 63°C.

We can estimate 10 to 20 years of outdoor weather resistance with a 10,000 to 20,000 hours test by S.W.M. and 30 years of outdoor weather resistance with 2,000 hours test of SUV.

S.W.M. SUV

Figure 1 Accelerated weather durability test machine. S.W.M. and SUV

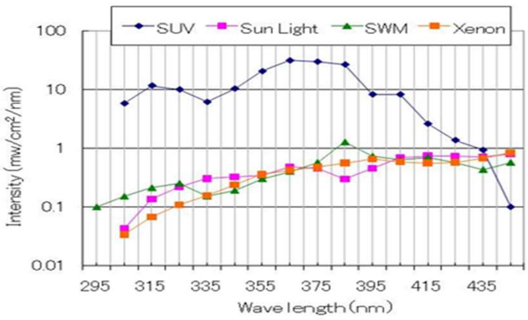


Figure 2 Distribution of radiation intensity

Table 1 Test conditions and acceleration factor for weather durability acceleration tests

accelerated weather	S.W.M.	Metal halide (SUV)
UV Radiation (W/m^2)	79	1500
Test period (hours) equivalent 10 years outdoor exposure =3000MJ/m^2	10500	660
Time for one cycle(min)	60 minutes	12 hours 20 seconds
one cycle progress	con1→con2	con1→con3→con2→con3
Condition1	Light / 48 minutes	Light / 10 hours
Condition2	Light & rain / 12 minutes	Dark dew / 2 hours
Condition3	-	shower / 10 seconds
Temperature at lighting	BP.63℃	BP.63℃

2.2 Outdoor exposure test locations

Outdoor exposure test locations are Japan and Florida, USA. The agricultural film is from Maitama City, Ibaraki Prefecture, Japan. Other exposed locations include Itoman City, Okinawa Prefecture, Nangoku City, Kochi Prefecture, and Ichihara City, Chiba Prefecture. Figure 3 is a photo of outdoor exposure sites in Okinawa and Kochi prefectures.

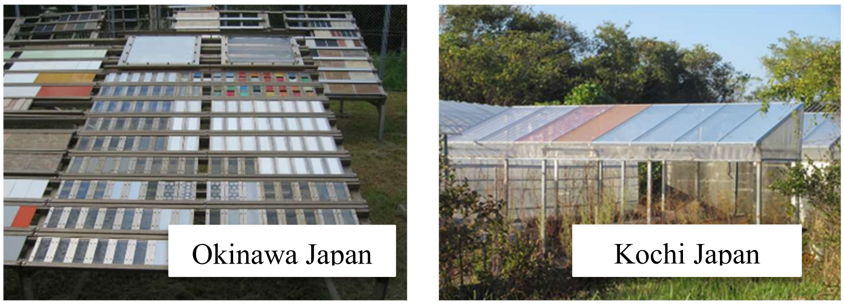


Figure 3   Outdoor Exposure Locations

3. Outdoor Exposure Results

3.1 Normal 60µm ETFE film outdoor exposure in Japan

In Japan, 60µm film has been used as a covering material for greenhouses since 1988, and it is still used 35 years later. In Europe, there are many greenhouses in which ETFE film has been used for 25 years. NIPPON CARBIDE INDUSTRIES CO., INC. in Japan first started selling the ETFE film "Natural Light F Clean" as a covering material for greenhouses. Currently, this film is being used in Ibaraki Prefecture in 2024. A photograph of this house is shown in Figure 4. The optical properties and transmittance chart of the film in the early and 35-year years are shown in Figure 5. After 35 years, there is data before and after cleaning the film. If you look at Figure 6, you can see that moss has grown on the film. In 2023, there were many complaints of moss staining greenhouses in eastern Japan. The transmittance has decreased by about 4%, and the haze has increased by 16%. If the dirt is removed with water, we find that the haze increases by 3% due to friction with sand and pebbles. Visible light transmittance and sunlight transmittance decrease by less than 1%. Table 1 shows the mechanical properties of the film. The breaking strength and elongation at break have been reduced by 7%, but there is no decrease in stress at the time of 10% strain. In fact, it is about 7% higher.

Figure 4   Photograph of a 60 µm ETFE greenhouse in use since 1988

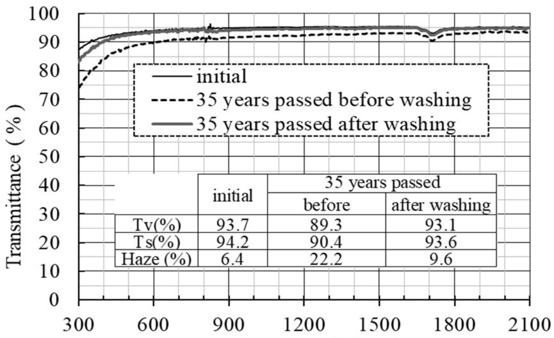


Figure 5   Optical properties of 60µm of ETFE film after 35 years outdoor exposure.

Figure 6   Pictures of the film before and after washing with water.

Table 2 Mechanical properties of 60 μ m ETFE film after 35 years outdoor exposure in Japan

	Standard	2023 measured (35 years later)	Initial (1987)
Strength to break	*JIS K7127	55.5 MPa	60.0MPa
Elongation to break	JIS K7127	358%	406%
Tear Strength	JIS K7128	203 N/mm	214 N/mm
Stress at 10% strain	JIS K7127	23.0	21.4

*JIS No. 1 dumbbell, pulling speed 200mm/ min

3.2 Clear 200µm, 500µm silver print in Japan

Clear films of 200µm have been exposed in Kochi Prefecture in Japan since 1997, and their mechanical properties have been measured 20 years after exposure in 2017. Table 3 shows the changes in the mechanical properties. Although the breaking strength has been reduced by 9%, the stress at the time of 10% elongation, which is important for design, has not decreased, and the initial value has been maintained. In addition, 500µm Silver Print products have been exposed since 2015 in Kochi Prefecture in Japan and the mechanical properties after 5 years in 2020 are measured. The results are shown in Table 4. The stress at the 10% strain tended to increase.

Table 3 Mechanical and Optical properties of ETFE 200NJ (20years outdoor exposure)

	Standard	1997: initial		2017: 20yers		Retention	
		MD	TD	MD	TD	MD	TD
Tensile Strength at break (MPa)	ISO 527-3	66.4	66.9	61.3	59.8	92%	89%
Tensile Strength at 10% Strain (MPa)	ISO 527-3	21.3	21.1	22.9	20.5	108%	97%
Elongation at break (%)	ISO 527-3	445	449	451	457	101%	102%
Tear strength (N/mm)	JIS K 7128-3	196	196	211	212	108%	108%
Transmittance of visible light (%)	DIN EN 410	88.9		88.4		-0.5%	
Haze (%)	JIS K 7136	14		16		+2%	

Table 4 Mechanical and properties of ETFE 500NJ print (5 years outdoor exposure)

	Standard	2015: initial		2020: 5yers		Retention	
		MD	TD	MD	TD	MD	TD
Tensile Strength at break (MPa)	ISO 527-3	65.4	66.6	59.0	60.6	90%	91%
Tensile Strength at 10% Strain (MPa)	ISO 527-3	20.1	19.2	21.9	21.2	109%	110%
Elongation at break (%)	ISO 527-3	437	468	427	459	98%	98%
Tear strength (N/mm)	JIS K 7128-3	189	188	198	198	105%	105%

In the ETFE exposure test, the breaking strength decreases when it undergoes a photoactivation reaction of titanium oxide, as stated by Aruga [1]. Visually, the dispersed titanium oxide particles in ETFE, aggregate and the film becomes whiter than before exposure, making it easy to determine whether it has been photocatalyzed. In the example observed in Japan, the breaking strength decreased by about 20% after 12 years of exposure. However, the stress at 10% elongation did not decrease. This phenomenon occurred when titanium oxide, which has low weather durability, was used as pigment.

3.3 Normal and functional ETFE films in Florida

3.3.1. Mechanical properties

The 200µm film has been undergoing outdoor exposure testing in Florida since 2006. The most recent data is 15 years after start of exposure. The next measurement of mechanical properties will be in 2026. As mechanical properties, we measure strength at break, elongation at break, strength at 10% strain, and tear strength. We also measure optical properties. The characteristics of the seven test films are as follows. 200WT (transparent white), 250TB (transparent blue), 200UVC (UV cut), 200NJ (normal ETFE), 200NJ print (200NJ silver printing ink), 200IRC (near infrared light absorption), 200ME (higher 10% strain type). 200ME uses a modified resin to obtain higher stresses at 10% strain, while another film is made with AGC's regular ETFE type. Figures 7 to 10 show the change of strength at break, elongation at break, strength at 10% strain, and tear strength. Strength at break, elongation at break, and tear strength are maintained at over 95%. The stress at 10% strain increases by 5%, similar to the results of outdoor exposure in Japan.

In Florida, 25NJ, 50NJ, 100NJ, and 50HJ (single-sided matte finish) are tested in the same way. These are thin films of 25µm to 100µm used as surface materials for flexible solar cells. The tendency after 15 years of exposure is the same as that of thick films. Strength at break, elongation at break, and tear strength maintain approximately 95 to 100%, and stress at 10% strain increases by 5%. Over a period of about 15 years, there is no difference in deterioration depending on the thickness, and there is no deterioration at all.

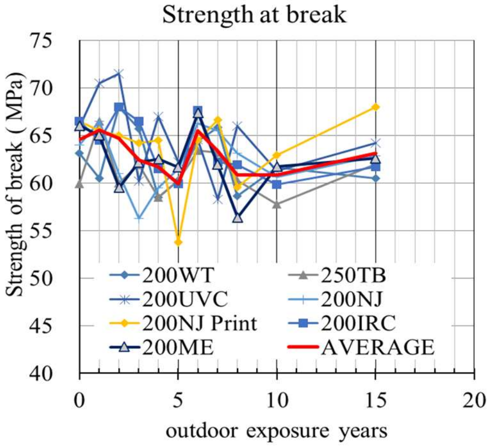


Figure 7 Change of at strength at break at outdoor exposure in Florida.

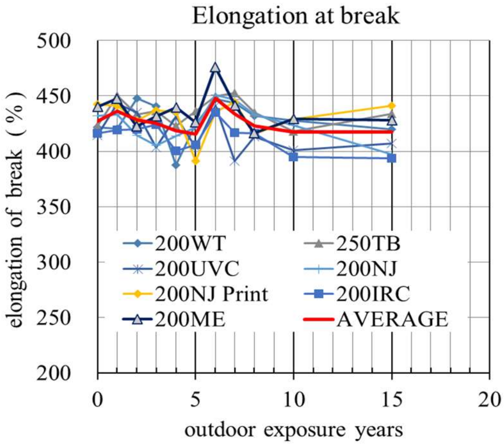


Figure 8 Change of stress at elongation at break at outdoor exposure in Florida.

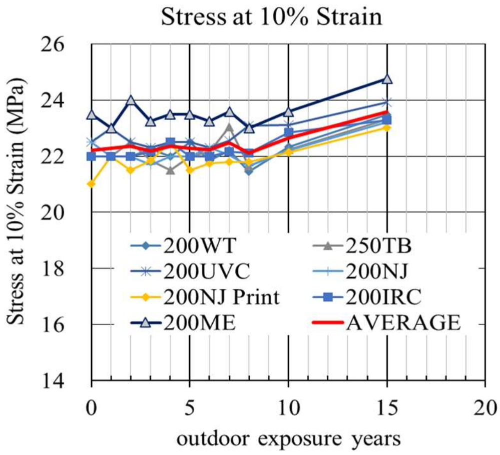


Figure 9 Change of stress at 10% strain at outdoor exposure in Florida.

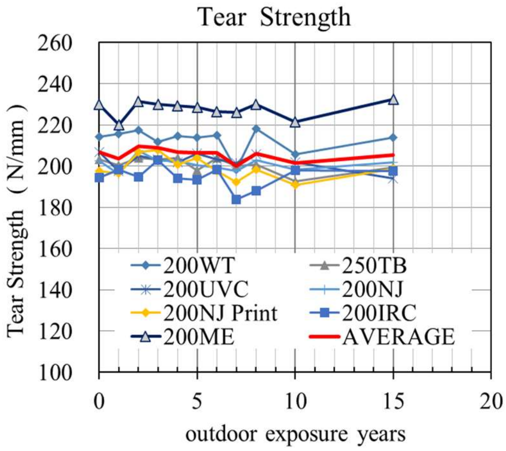


Figure 10 Change of at tea strength at outdoor exposure in Florida.

3.3.2. Optical properties

The optical properties of 200IRC, 200WT, 250TB, 200NJ, etc. do not change at all after 15 years of exposure in Florida. However, only in the UV blocking film 200UVC, changes were observed after 15 years. Note that the mechanical properties remain unchanged as shown in 3.3.1. The optical chart is shown in Figure 11. There are few changes up to 10 years, but after 15 years, the UV protection function has been halved. Figure 12 shows the SUV test results for the film being tested in Florida. According to the SUV results, it is calculated that the transmittance at 300nm will reach 41.9% after 20 years (1350/660=20), but it actually happened after 15 years. Although the acceleration factors are not perfectly matched, there is a strong correlation between SUV testing and outdoor exposure. The 2022 improved version has an improved UV cut filler shown in Figure 13. The surface hydrophobic agent has been changed to one with higher hydrophobic performance. As a result of this effect, we were able to invent a film that maintains its UV blocking function for a longer period, as shown in Figure 12.

Figure 13 shows the filler (CeO2:SiO2=40:60) developed by AGC. It has a three-layer structure of cerium oxide, silica, and a hydrophobic agent. Coating silica prevents HF from attacking CeO2, so silica coating is effective in improving weather resistance, as stated by Aruga et al. [2]. When UV absorbing filler is attacked by a small amount of hydrogen fluoride (HF), it becomes cerium fluoride and loses its UV absorption function. This HF is generated when ETFE film is formed. It can also be caused by ultraviolet rays hitting the ETFE from the sun.

Additionally, an ETFE film that completely blocks UV light below 360nm has been achieved by newly synthesizing a silica-coated zinc oxide filler and blending it into ETFE. Haze is 10% with 100μm film. Currently, after 11 years of exposure in Kochi Prefecture, Japan, the optical properties have not changed. It is shown in Figure 12. Unfortunately, it looks whiter than regular ETFE.

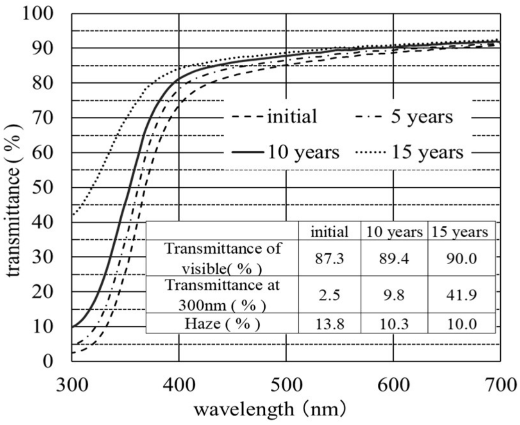


Figure 11 Optical property of 200um UV blocking ETFE film at Florida exposure

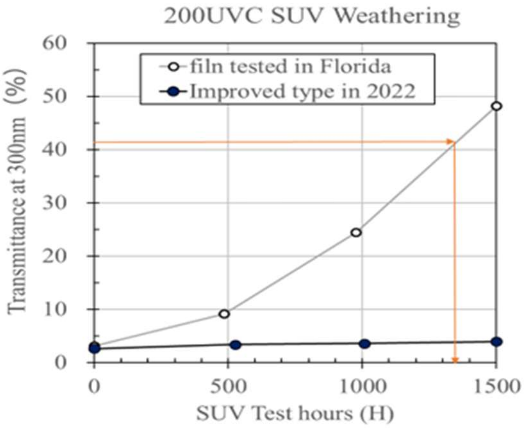


Figure 12 SUV test results for the film being exposed in Florida and improved type.

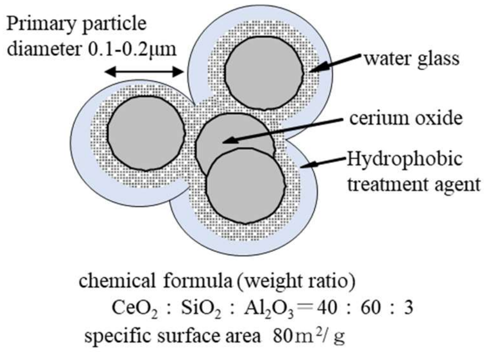


Figure 13 Silica coating cerium oxide filler for UV blocking

Figure 14 Exposure Test of UV-blocking Film using Silica-coated Zinc Oxide filler.

3.4 Weather durability test results of printing inks

3.4.1 Effects of printing ink

In terms of glass, functional glasses such as LOW-E glass, which allow light to pass through but block heat, have been developed by sputtering a thin metal layer. However, films for ETFE membrane structures, which expand and contract due to heat and load, have not yet been put to practical use. Figure 12 shows the relationship between visible light transmittance and solar heat gain rate of an ETFE film with adjusted thermo-optical properties. There are films that selectively absorb near-infrared rays from 780nm to 2500nm, but since they are not reflective, the SHGC is only slightly lower. Therefore, there is no such thing as a bright but cool film. Therefore, thermal control is based on two methods: coloring and printing ink. The ink material used is aluminum, which has reflective properties in all wavelengths from UV to visible to infrared rays, or titanium oxide, which reflects UV to visible light. The printing method is to perform electric discharge treatment on ETFE film to increase wettability, and then print using gravure printing. Table 4 shows the thermal and optical properties of the printed film when silver ink was printed on 250μm ETFE.

The printing design is free, and by changing the printing area, it is possible to obtain the visible light transmission and S.H.G.C. specified for the building itself.

The thickness of printing ink is usually about 2μm, and it is usually placed inside the cushion method, but it is also used in a single-layer tension style.

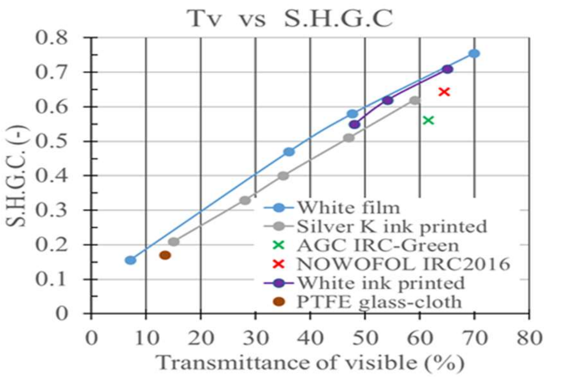
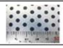
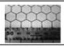
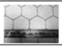


Figure 15 Relation od Visible light transmittance and solar heat gain coefficient

Table 5 Light, thermal characteristics of printed film

Base film	250NJ				
ink	High reflection silver K				
Print pattern name	K46D16	K63D04	K80N04	K90X13	K96X34
print area(%)	46	63	80	90	96
Figure					
Pattern character	16mm dot	4mm dot	4mm nega dot	middle hexagon	large hexagon
Transmittance of visible	59	47	35	28	15
Reflectance of visible	30	39	47	52	61
Transmittance of solar	60	47	35	28	15
Reflectance of solar	30	39	48	53	62
Transmittance of UV	53	43	32	26	14
Reflectance of UV	33	39	44	48	60
SHGC (Inside: Printed surface)	0.62	0.51	0.4	0.33	0.21
SC (Inside: Printed surface)	0.71	0.58	0.45	0.37	0.24
U(W/m²·K) (Inside: Printed surface)	5.6	5.4	5.2	5.0	5.0

3.4.2 Results of weathering accelerated tests and actual exposure tests in Japan for printed ink.

Figure 16 shows an example where printed ETFE was used in a single layer . Figure 17 shows the results of an actual exposure test (back exposure) performed on the printed film used in Figure 16 in Kochi Prefecture, Japan. After 18 years of exposure, the reflectance retention rate is 77%. Further, the results of accelerated weathering test (S.W.M.) of the same film are shown in figure 18. From the cumulative amount of UV radiation, it can be calculated that 1000 hours of S.W.M. testing is equivalent to one year of outdoor exposure, but they do not match. However, there is a correlation between Figure17 and 18. The decrease in reflectance is caused by the dissolution of aluminum particles in the ink by water containing hydrofluoric acid. By developing aluminum particles that are less susceptible to the effects of these decomposition products, we have been able to develop a printing film as shown in Figure 19. After 20 years of outdoor exposure, the reflectance maintenance rate can be expected to be around 90%.

Figure 16 Printed ETFE films

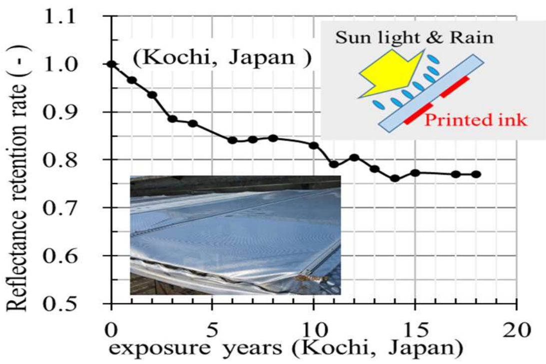


Figure 17 The result of outdoor exposure test about printed ink in Kochi. Japan.

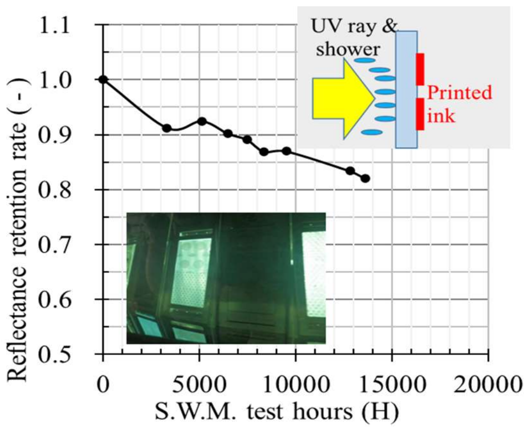


Figure 18 The result of weather durability test (S.W.M) for printed ink.

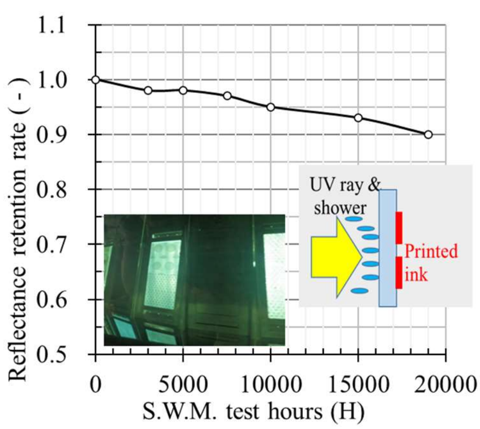


Figure 19 The result of weatherability test (S.W.M) for improved ink.

4. Summary

Actual exposure results have confirmed that the lifespan of ETFE is 35 years or more in Japan, assuming that it is the retention period of stress at 10% strain. After 35 years in Japan, the stress at 10% strains of a 60μm film not only maintained its initial value but also increased by 5%. This trend was also observed in 200μm film exposed for 20 years in Japan. Films with different thermal and optical properties by adding fillers or printing were also exposed in Florida for 15 years. The results showed that the stress at 10% strain of all films increased. Therefore, at present, there is no film that can be judged to have reduced stress at 10% strain in outdoor exposure tests.

In terms of optical properties, the UV blocking function of the UV blocking film suddenly changed after 15 years of exposure in Florida and 18 years of exposure in Okinawa, decreasing by half. Furthermore, silver print film showed 23% decrease in reflectance after 18 years of single-layer outdoor exposure in Kochi Japan. A small amount of decomposition products generated from ETFE dissolve the cerium oxide in the UV blocking film and the aluminum in the silver print, but these changes in optical properties do not affect the mechanical properties of ETFE.

Most of the data in this paper is for films manufactured more than 15 years ago. We hope that by synthesizing a filler that is resistant to decomposition products from ETFE, we will be able to provide an ETFE film those optical properties will not change for more than 30 years.

5.References

[1] Hiroshi Aruga. Expansion of application for the membrane structure using ETFE film, Res. Reports Asahi Glass Co., Ltd., 65(2015),35-45.

[2] Hiroshi Aruga, Yasuyo Nishimura, Yasuhumi Fukumoto, Development of the Weather-Resistant Agricultural UV-blocking ETFE Film, Journal of the Society of Agricultural Structures, Japan 44(4), 174-183, (2013)