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.)

Microscopic characterization of weathering aging ethylene tetrafluoroethylene (ETFE) foils

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Abstract
The material properties of ETFE foils after aging in natural environment are the basis for long-term performance evaluation of ETFE building structures. In this paper, the aging ETFE foils used in an experimental mockup for more than 13 years were selected to carry out the micro experiments. The micro experiments include SEM for morphology, XRD for degree of crystallinity and crystallite size, DSC for crosslinking of the polymer and FTIR for functional groups. The experimental results show that the rough surface morphology and many apparent wrinkles existed for the aging ETFE foils. The degree of crystallinity of aging ETFE foils only increased by 2.9% while the crystallite size of the aging ETFE foils increased by 7.8% in comparisons with those of new ETFE foils. However, no significant degradation was observed for the crosslinking of ETFE polymer and the change of functional groups. Therefore, the research results are believed to be significant for the maintenance and safety-evaluation of ETFE building structures.

Keywords: ETFE foil, membrane structure, microscopic characterization, aging performance

1. Introduction
Ethylene tetrafluoroethylene (ETFE) is an excellent copolymer material used in the building industry. ETFE foils with chemical resistant to acids and alkali and non-stick properties make themselves self-cleaning. The high light transmittance within the range of 90-95% can increase light and thermal performance. The lightweight and recyclable performance meet the demands of green buildings. Therefore, the use of ETFE foils as building roofs or facades have attracted considerable attention in recent decades [1], such as Haneda airport terminal in Japan and Suoyuwan football stadium in China.

As a building material, the long-term performance evaluation of ETFE structures rely on material properties because the duration of ETFE structures is about 30 years [2, 3], where the environmental factors affect the micro structures and thus macro properties. Zen et al. focused on the radiation-induced crosslinking and degradation of ETFE films. The changes in the degree of crystallinity and the intensity of crystalline peak were obtained when compared to the pristine polymer [4]. Nasef et al. analyzed the electron beam irradiation effects on ethylene-tetrafluoroethylene copolymer films [5]. Hao et al. focused on the electron and gamma irradiation-induced effects in ethylene-co-tetrafluoroethylene films, showing that the microstructure changes are in the bulk and on the surface [6]. Moreover, The artificial weathering study on the degradation in encapsulant transmittance shows no catastrophic cracking but modest degradation of the transparent backsheet [7]. Flueler and Aller reported the long-term expectations and experiences of ETFE membrane construction. A new classification system connected to public register was introduced to assess the hail impact resistance [8]. Paolinia et al. investigated the natural ageing effect on solar spectral reflectance of roofing membranes of commercial buildings in Italy [9].

The aging performance of ETFE foils depend on the reduced material performance while these properties of ETFE foils are not well-addressed in the literature due to the lack of aging materials. Hu et al. designed an experimental mockup of ETFE cushions and used it as an experimental setup [10], which has been used for more than 13 years. Therefore, the analysis of the ETFE foils of the demolished mockup can give some understanding of the aging performance. The mockup experienced the combination of high and relative humidity, meaning that the aging time of the ETFE foils are longer than expected [11]. Therefore, this study aims to understand the material performance of aging ETFE foils with micro experiments, which are essential properties for the evaluation of structural behavior.

The composition of this paper is organized as follows. The aging ETFE foils are given in Section 2 and the microscopic experiments and analysis are described in Section 3. Finally, typical observations and useful values are summarized in the Conclusions.

2. Materials

The materials used in this study are 200μm ETFE foils purchased from the commercial market, see Fig. 1. This thickness is in the suitable range used as building materials. The material was used for an experimental mockup to investigate the electrical-thermal-structural performance of PV-ETFE cushion, simulating the Japan Pavilion and other PV-membrane projects. The experimental mockup was used until 2017 and then exposed to the environment until 2023. Therefore, the service period of the ETFE was more than 13 years. In fact, the PV can generate high temperature that accelerates the aging of ETFE foils. In this case, the demolished ETFE foils from the experimental mockup are used to investigate the aging performance.

The measurement of the aging ETFE foils for 10 specimens show that the average thickness of the aging ETFE foils is 216 um, which is increased by 8%. Moreover, to obtain the material performance, the micro experiments are indispensable for the values.

Fig. 1 (a) Aging ETFE foil, (b) New ETFE foil

3. Microscopic characterization

The micro structures of the aging ETFE foils could be changed in the long service period exposed to the environment. In this study, the SEM, DSC, XRD and FTIR experiments are used to quantify and quantify the micro structures.

The SEM experiments are used to characterize the surface and cross-section of the ETFE foils. The dimensions of the specimens are 1cm×1cm, which is coated with gold on the surface to increase the conductivity for high resolution images. The equipment Sirion 200 was utilized to carry out the experiments. Moreover, the SEM experiments for the new 200um ETFE foil are performed to compare the micro characteristics of the aging ETFE foils.

The experimental results of the surface and cross-section of the ETFE foils are given in Fig. 2 and Fig. 3. It is obtained that the surface of the new ETFE foils is smooth and only very few small granules exist. However, the surface of the aging ETFE foils shows a large amount of larger granules and scratch as well as valley and wrinkles on the surface. The unsmooth surface can affect the light transmittance and the thickness of the materials. For the cross-section surface, the surface of the new ETFE foils is smooth while the surface of the aging ETFE foils presents the apparent valley and mountain. The change of the micro structure can result in the change of macro mechanical properties, meansing that the micro and macro experiments are both necessary to analyze the material performance of the aging ETFE foils.

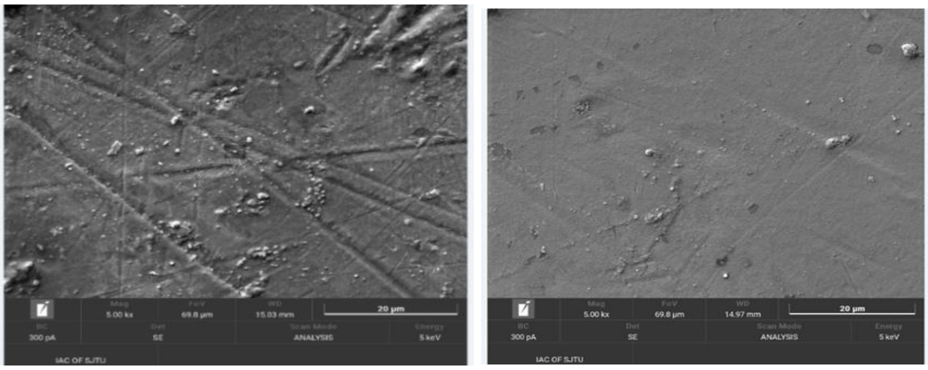


Fig. 2 SEM experimental results of material surface: (a) Aging ETFE foil, (b) New ETFE foil

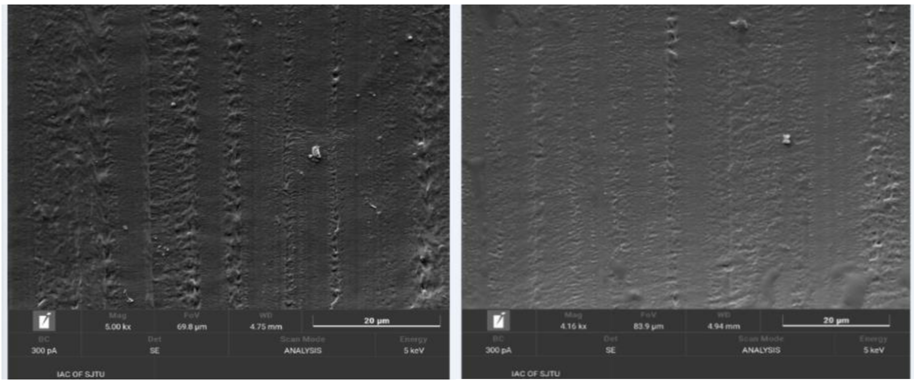


Fig. 3 SEM experimental results of material cross-section：(a) Aging ETFE foil, (b) New ETFE foil

For the XRD experiment, it is utilized to assess the crystalline and crystallite size. These material properties are related to the mechanical properties based on the polymer theory. For these reasons, the X-ray diffraction are used to characterize the crystalline and crystallite size. The crystallite size can be determined with the following equation.

$$D = \frac{K\lambda}{\beta cos\theta} \tag{1}$$

where D is crystallite size, K is Scherrer constant, λ is the wave length of the X-ray beam used (1.54,184 Å), β is Full width at half maximum (FWHM) of the peak, θ is the Bragg angle. Scherrer constant denotes the shape of the particle and its value is most commonly taken as 0.9. Meanwhile, the XRD equipment is utilized to characterize the new ETFE foils. The experimental results of XRD experiment are summarized in Table 1. It is obtained that the degree of crystallinity of the aging ETFE foils only increased by 2.9% while the crystallite size of the aging ETFE foils increased by 7.8%. According to the polymer theory, the material strength decreases with the increase of the crystallite size, meaning that the macro mechanical properties decrease.

The DSC experimental results can quantify the crosslinking of the polymer materials. A common way to calculate the heat of the specific mass from the areas of the DSC curves. The DSC curves of the new and aging ETFE foils are illustrated in Fig. 5. The results show that the crosslinking degree of the new and aging ETFE foils are 67.9 W/g and 65.1 W/g, i.e. the reduction ratio is 4.5%, which suggests that the crosslinking performance of the aging ETFE is not significant.

Table 1 Degree of crystallinity and crystallite size of ETFE foils

Materials	Degree of crystallinity %	Crystallite size/nm
New ETFE foil	61.1	3.01
Aging ETFE foil	62.9	3.25

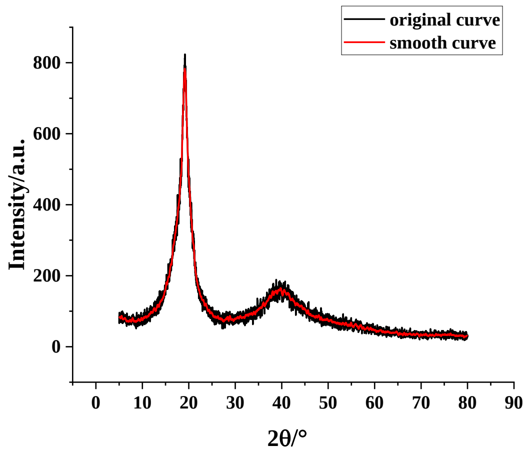
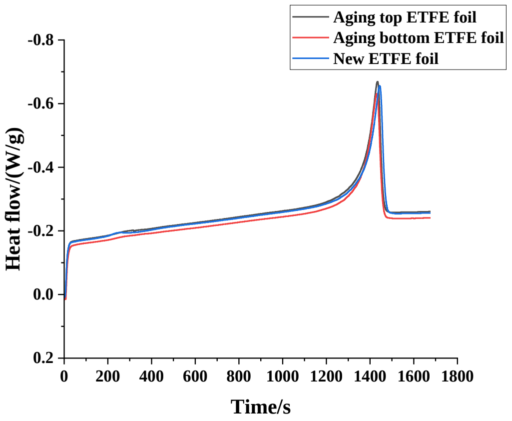


Fig. 4 XRD experimental results of aging ETFE foils



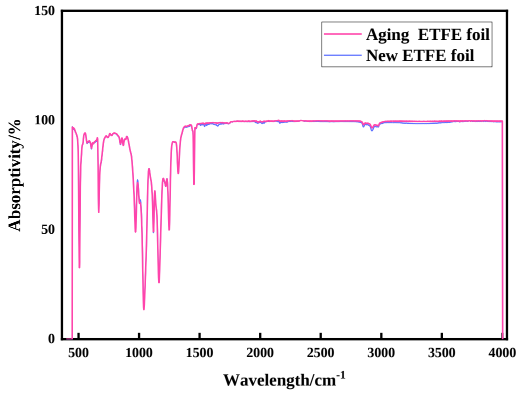


Fig. 5 DSC experimental results

Fig. 6 Experimental results of infrared spectroscopy

The FTIR experiments can characterize the functional groups that show the change of oxidizing reaction of carbon atoms and the aging performance of the materials. In this study, the Nicolet 6700 is used to perform the FTIR experiments and the results are illustrated in Fig. 6. The comparisons between these curves show that that there is no remarkable difference between them, indicating that the ETFE foil has good performance exposed to the environment for a long time.

4. Conclusions

This paper focuses on the micro properties of the aging ETFE foils demolished from an experimental mockup that was used for 13 years. The micro morphology, degree of crystallinity and crystallite size, crosslinking of the polymer and functional groups were quantified with SEM, XRD, DSC and FTIR experiments. The typical observations and useful values are summarized as follows.

- The surface of the aging ETFE foils shows many large granules and scratches as well as valley and wrinkles.
- The degree of crystallinity of the aging ETFE foils only increased by 2.9% while the crystallite size increased by 7.8% in comparisons with those of new ETFE foils.
- No significant degradation was observed for the crosslinking of the polymer and the change of functional groups.

This paper extends the study on the micro material performance from new ETFE foils to aging ETFE foils. These results and conclusions are useful for the maintenance and safety-evaluation of ETFE building structures.

Acknowledgements

The work was supported by Shanghai Pujiang Program (No. 22PJ1405600). The authors are grateful to the editors and anonymous reviewers for the comments and suggestions in improving the quality of the paper.

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