



**HAL**  
open science

## Degradation of PVDF-HFP Matrix

Fanon Julienne, Emmanuel Richaud

► **To cite this version:**

Fanon Julienne, Emmanuel Richaud. Degradation of PVDF-HFP Matrix. *Macromolecular Symposia*, 2022, *Times of Polymers and Composites (TOP)*, 405 (1), pp.2100223. 10.1002/masy.202100223 . hal-04073510

**HAL Id: hal-04073510**

**<https://hal.science/hal-04073510v1>**

Submitted on 18 Apr 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Degradation of PVDF-HFP Matrix

Fanon Julienne and Emmanuel Richaud\*

This paper explores both physical ageing of polyvinylidene fluoride (PVDF) and its copolymers with hexafluoropropylene (HFP). Water ageing and annealing are shown to have a negligible influence on mechanical properties. Chemical ageing is thus expected to be the main source of long-term degradation. The nature of associated chemical trackers is discussed but it seems clear that their fraction is very slow for low temperature thermal ageing.

DSC measurements were performed on a Q1000 DSC at 10°C mm<sup>-1</sup> with standard aluminum pans and lids. The thermograms were then processed under TA Universal Analysis. The crystallinity ratio of the initial and aged polymers was calculated on the DSC thermograms, comparing the theoretical heat of fusion of 100% crystalline PVDF<sup>[4]</sup> and measured heat of fusion (linearly between 62.5 and 190°C, with the TA Universal Analysis software):

## 1. Introduction

Recently, a growing interest has appeared in the use of polyvinylidene fluoride (PVDF), ranging from filtration membranes (waste water, viruses...), to electromechanical devices, etc.<sup>[1]</sup> PVDF with a certain number of other monomers such as hexafluoropropylene (HFP) can modify morphological characteristics and create attractive structures and physicochemical properties. Indeed, these copolymers have a high solubility, a low degree of crystallinity, and a low glass transition temperature.<sup>[2]</sup> On larger scales, they have good thermal properties and chemical inertness to acids and petroleum.<sup>[3]</sup>

The study of aging under controlled conditions makes it possible to better identify the degrading factors, to understand the effect of changes in molecular structure on mechanical properties, and finally to determine the degradation mechanisms.<sup>[1]</sup>

## 2. Experimental Section

Films PVDF and poly(vinylidene fluoride)-co-hexafluoropropylene (PVDF-HFP) with three different ratios of HFP (5%, 10%, and 15%) were obtained by a compression press process using commercial pellets supplied by Sigma-Aldrich.

The tensile tests were measured using H4 tensile specimens ( $l_0 = 10$  mm, width = 2 mm, thickness = 40  $\mu$ m), which were drawn at 10 mm min<sup>-1</sup> and 100 N by an Instron 4301 in a temperature and humidity-controlled room (respectively 23°C and 50 RH).

The sol-gel experiments were conducted by immersing approximately 10 mg of polymer in 4 mL of THF.

$$\chi = \frac{\Delta H_f}{\Delta H_f^0} = \frac{\Delta H_f}{1025}$$

FTIR spectra were acquired using a Fourier transform infrared system (x x x) in transmission mode. Measurements were realized with 10 analyses ranging from 4000 to 400 cm<sup>-1</sup>. The spectra were then baseline corrected with the software "Spectrum."

To understand the evolution of their properties during aging and their degradation mechanism, the study focused on three significant examples of ageing: (i) annealing, (ii) impact of water, and (iii) chemical aging.

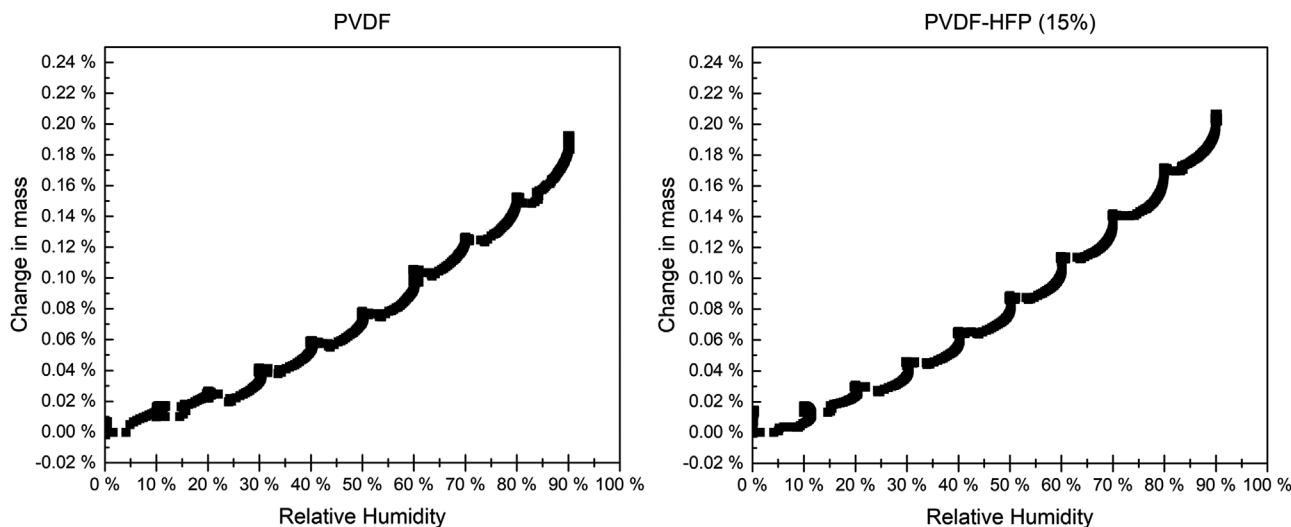
A study on the mechanisms of polymer-water interaction (sorption, diffusion) by DVS was started for a test temperature of 80°C, with steps ranging from 0% to 90% RH from 10% to 10%. To evaluate the stability toward relative humidity, tensile specimens as well as a control were also placed in ultrapure water at 80°C. In order to observe the consequences of water permeation tensile test was performed.

Annealing in air at 140°C after 1 week and chemical aging at three different temperatures, 140°C, were also analyzed by placing tensile specimens in ovens. Samples of both ages were characterized at different scales: (i) molecular (FTIR), (ii) macromolecular (sol-gel dilution), (iii) microstructure (DSC), and (iv) mechanical properties (traction).

### 2.1. Stability Toward Relative Humidity

A study on the polymer-water interaction mechanisms by dynamic vapor sorption (DVS) was carried out. The curves obtained on PVDF and PVDF-HFP (15%) given in **Figure 1** showed very low water absorption (<0.25%), which was perfectly corroborated by the literature.<sup>[1,5]</sup>

Once the mass of the control sample was stabilized, in order to observe the consequences of the permeation of water on the mechanical properties, the mechanical properties of the model films before and after immersion in 80°C in distilled water were compared. **Figure 2** presents the modifications to the Young modulus, yield stress/strain, and ultimate tensile stress/strain which seem



**Figure 1.** Sorption isotherm for initial (left) PVDF and (right) PVDF-HFP (15%). HFP, hexafluoropropylene; PVDF, polyvinylidene fluoride.

minor. It can be noticed here that the initial and final mechanical properties were proportional to the HFP ratio.

## 2.2. Physical Ageing by Annealing

After a week of aging in the air at 140°C, it was clear that the melting peaks in red in **Figure 3** were differed from the initial DSC thermograms. These variations in the shapes of thermograms, indicated by a small endotherm, started at a temperature close to the thermal treatment, which could suggest the presence of annealing.<sup>[6]</sup>

Regarding the first scan, a slight increase of the crystallinity ratio during the first 7 days of aging was observed. It could confirm the presence of an annealing. Indeed, the crystallinity increased from approximately 4.5% for PVDF and PVDF-HFP (5%), 3.5% for PVDF-HFP (10%), and 2.5% for PVDF-HFP (15%). Therefore, it seemed that the increase in the crystallinity ratio was all the more important as the level of HFP was low. Unlike the first scan, the second did not show any evolution of crystallinity which confirmed the fact that there was no macromolecular alteration, and it was considered that thermal ageing only resulted in morphological changes.

In order to see if annealing had an effect on a larger scale, the mechanical properties were investigated by tensile tests. **Table 1** shows a comparison of the mechanical properties before and after ageing in a 140°C oven for a week. In both cases, PVDF-HFP (15%) had large ductility ranges. The annealing did not weaken the polymer (**Table 1**). Little difference was found between the two conditions, suggesting that annealing did not weaken PVDF-HFP (15%).

## 2.3. Chemical Stability

As shown in **Figure 4**, it appeared that HFP promoted degradation and oxygen reduced the induction period. Unlike TGAs under oxygen, TGAs under nitrogen left a residue that might indicate a crosslinking. In addition to this, it should be noted that

PVDF-HFP (15%) was soluble in THF, but more the aging time was advanced and more it became insoluble. This further supported the possibility of crosslinking.

After 31 weeks of chemical aging at 140°C, no significant chemical changes were highlighted by FTIR (**Figure 5**). Indeed, one of the main markers of oxidation in infrared was the appearance of grouping in the carbonyl region (between 1560 and 1970  $\text{cm}^{-1}$ ). Nevertheless, the appearance of a peak in the region of 1515  $\text{cm}^{-1}$  was observed for PVDF-HFP (X), which appeared more important when HFP ratio increased and did not exist for PVDF.

The evolution of mechanical properties during chemical ageing was also be presented (**Figure 6**). Besides a slight change in behavior during the first 7 days (probably due to annealing), no major changes were observed thereafter.

## 3. Conclusion

To begin, very little water was absorbed by the four polymers (<0.25%), which is in agreement with the literature. With regard to annealing, the latter seems to be all the more important since the HFP rate is low. It was also found that there was no macromolecular change due to aging.

Whether it is annealing, thermal ageing, or wet aging, no significant change in mechanical properties has been noted. In conclusion, the ages tested in this study do not weaken, the PVDF and PVDF-HFP polymers are very stable.

Although during thermal degradation, the HFP causes an acceleration of the degradation of PVDF-HFP matrix, the PVDF-HFP with a higher content of HFP seems to have more interesting mechanical properties after aging. Finally, a probable cross-linking mechanism was identified.

Although during thermal degradation the HFP causes an acceleration of the degradation of PVDF-HFP matrix, the PVDF-HFP with a higher content of HFP seems to have more interesting mechanical properties after aging. Finally, a cross-linking mechanism was assumed to be present in the degradation of the polymers studied.

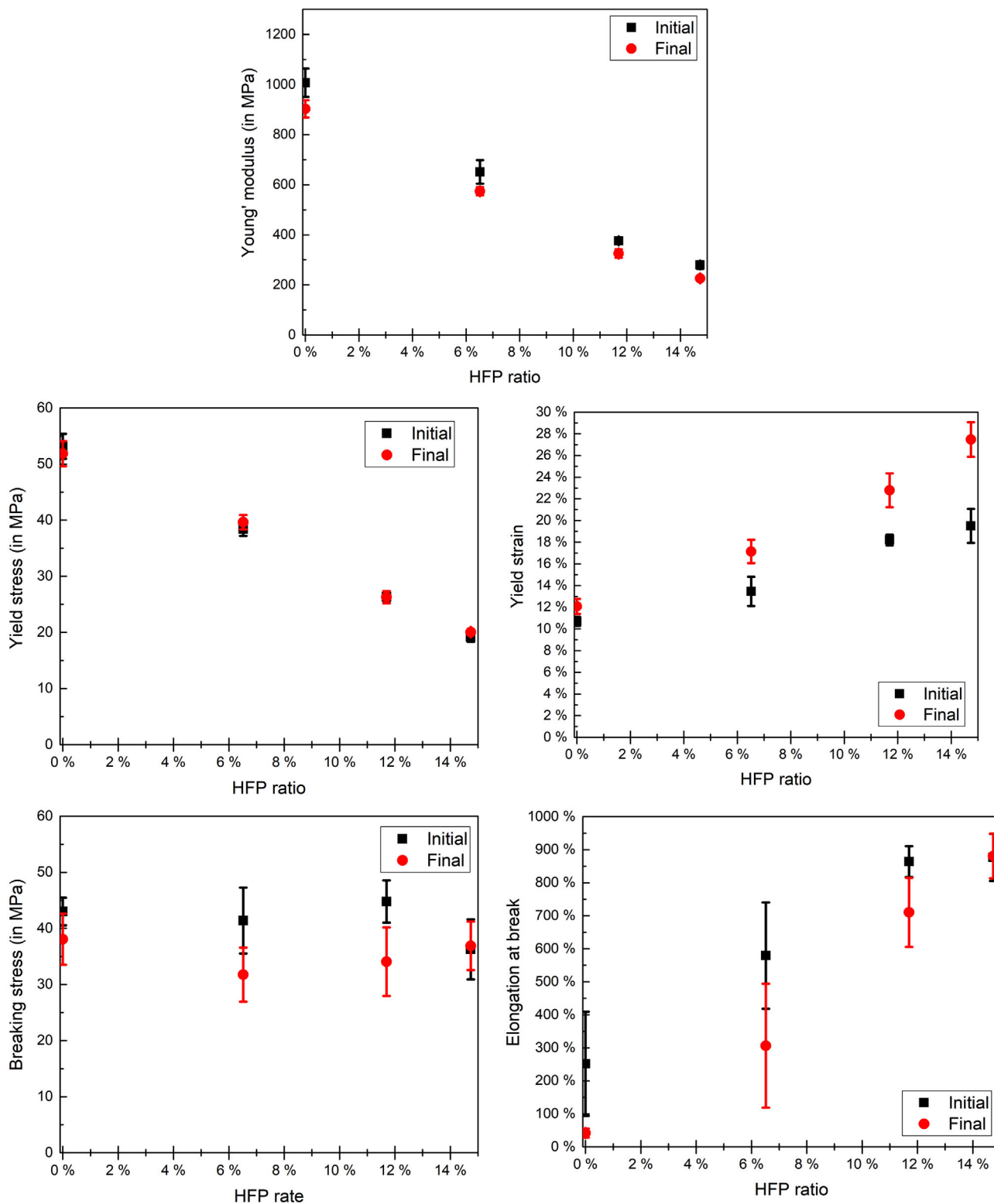
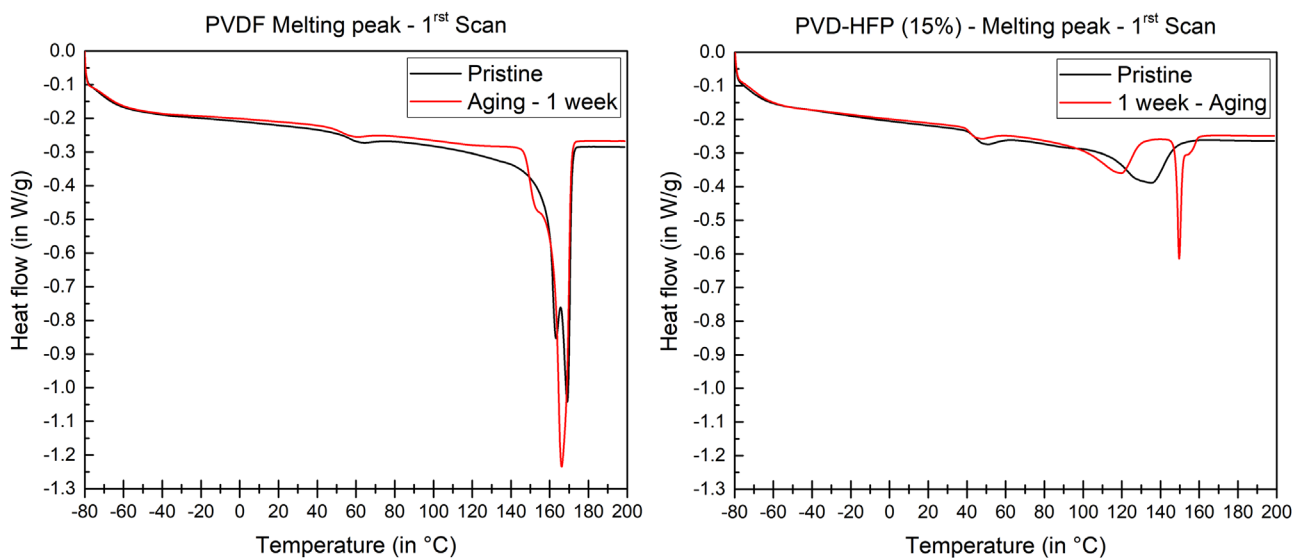


Figure 2. Comparison of the mechanical properties before and after immersion at 80°C during a week.



**Figure 3.** Comparison of thermograms before (black) and after (red) a week of aging at 140°C for PVDF (left) and PVDF-HFP (15%) (right). HFP, hexafluoropropylene; PVDF, polyvinylidene fluoride.

**Table 1.** Comparison of mechanical properties before and after annealing in air for a week.

Mechanical properties	PVDF-HFP (15%) – pristine	PVDF-HFP (15%) – aged: week 1
Young modulus [MPa]	301.54 ± 15.83	207.98 ± 73.14
Yield stress [MPa]	19.19 ± 0.86	16.53 ± 2.34
Yield strain	16.79% ± 1.24%	20.63% ± 3.19%
Breaking stress [MPa]	36.86 ± 4.59	39.22 ± 5.21
Elongation at break	728.64% ± 61.80%	970.80% ± 161.12%

HFP, hexafluoropropylene; PVDF, polyvinylidene fluoride.

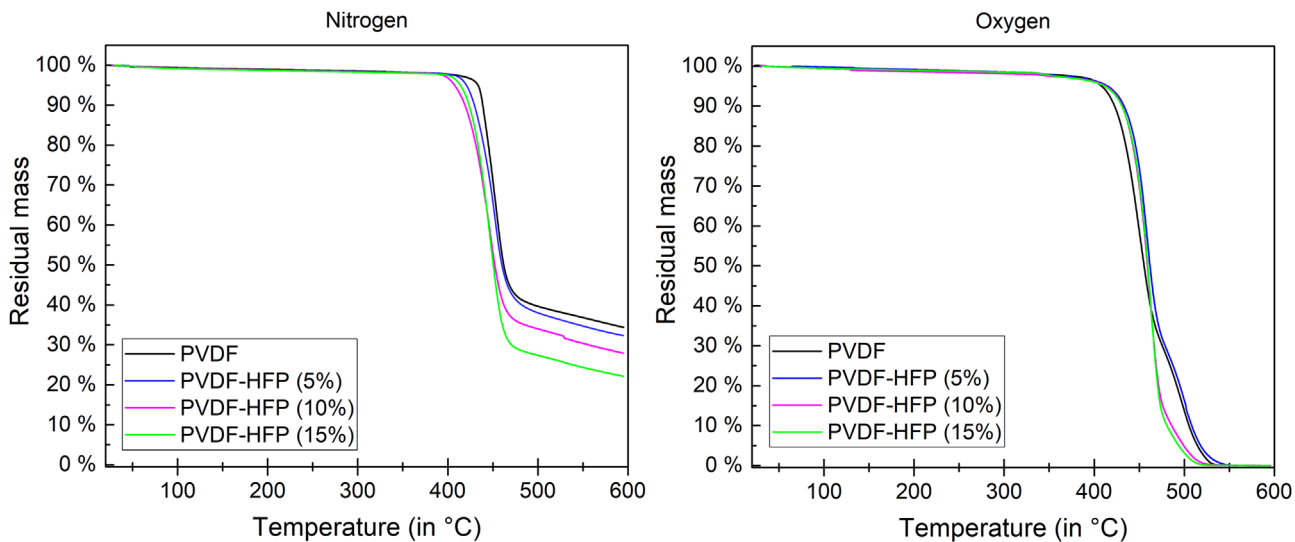


Figure 4. Anisothermal thermogravimetric analysis under (left) nitrogen and (right) oxygen.

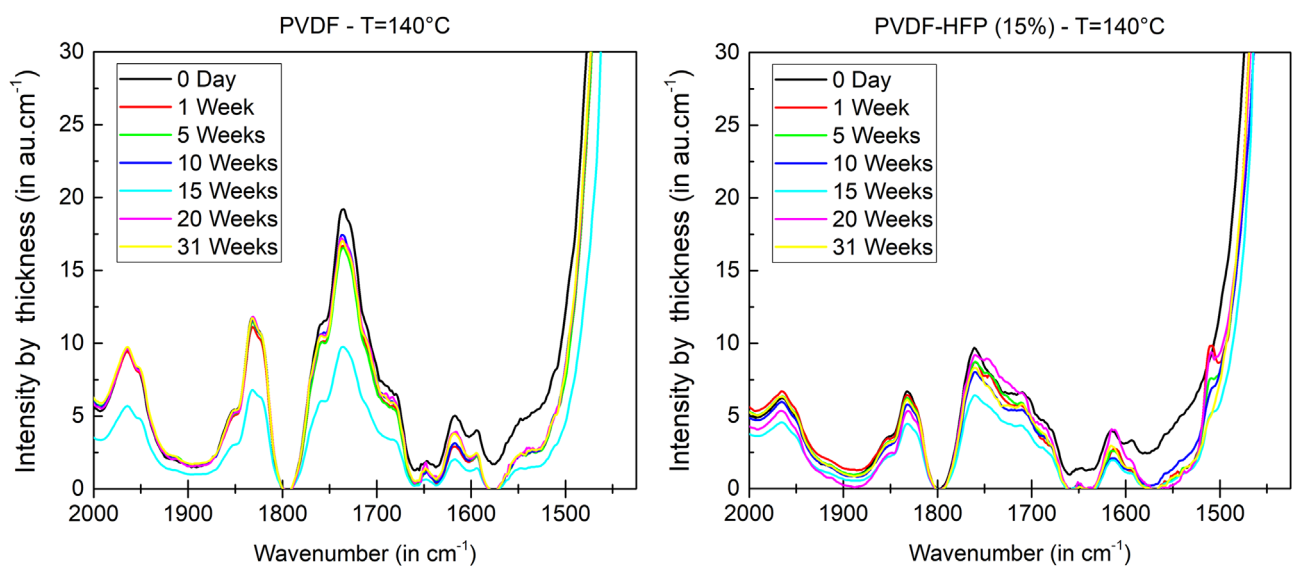
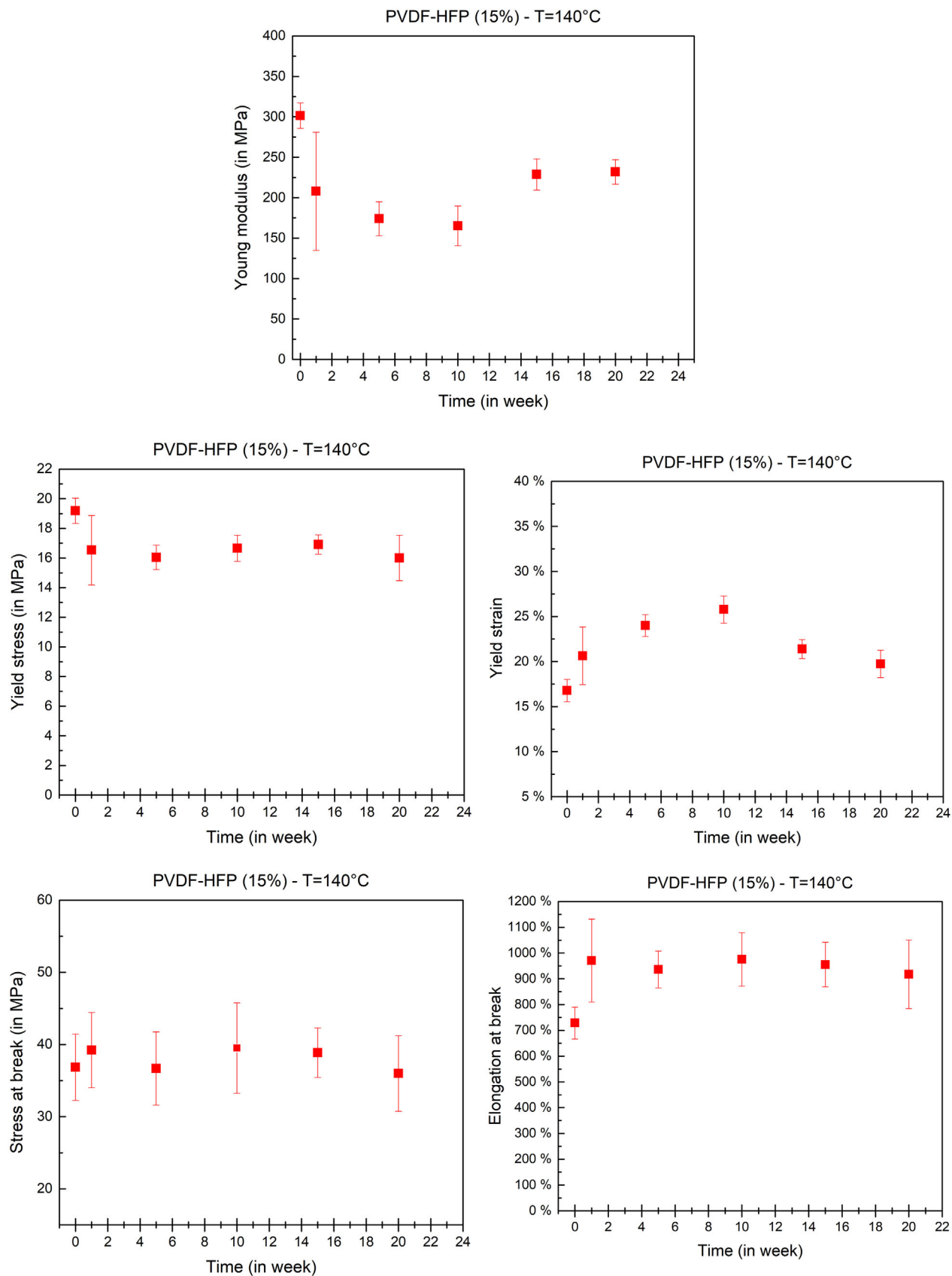


Figure 5. FTIR absorbance spectra of carbonyl group during chemical aging for (left) PVDF and (right) PVDF-HFP (15%). HFP, hexafluoropropylene; PVDF, polyvinylidene fluoride.



**Figure 6.** Evolution of the mechanical properties of PVDF-HFP (15%), during chemical aging at 140°C. HFP, hexafluoropropylene; PVDF, polyvinylidene fluoride.

## Keywords

ageing, annealing, crystallization, fluoropolymers

- 
- [1] J. Ravereau, A. Fabre, A. Brehant, R. Bonnard, C. Sollogoub, J. Verdu, *J. Membr. Sci.* **2016**, 505, 174. <https://doi.org/10.1016/j.memsci.2015.12.063>.
  - [2] Y. Yang, S. Ramalingam, G. Wu, S. L. Hsu, L. W. Kleiner, F.-W. Tang, N. Ding, S. Hossainy, *Polymer* **2008**, 49, 1926.
  - [3] M.-P. Gelin, B. Ameduri, *J. Fluorine Chem.* **2005**, 126, 575.
  - [4] A. Salimi, A. Yousefi, *Polym. Test.* **2003**, 22, 699.
  - [5] W. Li, H. Li, Y.-M. Zhang, *J. Mater. Sci.* **2009**, 44, 2977.
  - [6] Y. Furushima, A. Toda, C. Schick, *Polymer* **2020**, 202, 122712. <https://doi.org/10.1016/j.polymer.2020.122712>.