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Microstructural analysis of the microcavitation in PVDF after a thermo-diffuso-mechanical loading: competition between mechanical cavitation and gas plasticization

M. GERLAND, S.A.E. BOYER, S. CASTAGNET, G. BENOIT

Institut P' - Département de Physique et Mécanique des Matériaux, ISAE-ENSMA, UPR CNRS 3346
86961Futuroscope-Chasseneuil Cedex

Résumé :

Le polyfluorure de vinylidène (PVDF) sous fort chargement en traction s'endommage par superposition de deux effets : une déformation purement plastique et la création de microcavités dans la phase amorphe libre. De même, sous chargement de gaz, la diffusion des molécules gazeuses dans la solution gaz-polymère peut endommager la matrice polymère par création de cavités. Cette diffusion est surtout dommageable lors de la décompression du gaz. Il est ici question de discuter du rôle des interactions gaz-polymère sur la cavitation d'un PVDF sous chargement diffuso-mécanique. Les chargements en traction sont réalisés à 30 °C sous 4 MPa de deux gaz, l'hydrogène (H₂) et le dioxyde de carbone (CO₂). L'endommagement est estimé en quantifiant la fraction surfacique de cavités par analyses de micrographies électroniques à balayage (MEB) et en transmission (MET) après décompression. L'analyse structurale des échantillons endommagés sous traction/décompression est comparée à l'analyse structurale de l'échantillon non déformé et à celles des échantillons ayant seulement subi une décompression afin de pouvoir discriminer la cavitation issue de l'effet mécanique ou de la décompression de gaz. L'effet de l'hydrogène est moins sévère que celui du dioxyde de carbone car le dioxyde de carbone a pour effet d'augmenter la nucléation de petites cavités. D'un autre côté, le chargement en tension sous pression de gaz est plus sensible sous hydrogène comparé au dioxyde de carbone, ce qui est essentiellement lié à l'effet de plastification en compétition avec l'effet de cavitation. L'ensemble de ces analyses permet de poser une base à la compréhension des mécanismes d'endommagement par cavitation du PVDF sous chargement thermo-diffuso-mécanique.

Abstract:

Polyvinylidene fluoride (PVDF) under tensile loading damages by superimposition of a plastic deformation and a deformation induced by creation of micro-cavities in the free amorphous phase. In the same way, the study of polymers behaviour under gas loading shows that the gaseous molecules diffusing into the gas-polymer solution can damage the polymer matrix by cavitation creation. This diffusion is particularly damaging when the gas-polymer solution is subjected to the gas decompression. In this study, we discuss about the role of the gas-polymer interactions on the cavitation of a PVDF under a diffuso-mechanical loading. Tensile loadings are performed at 30 °C under 4 MPa of two gases, hydrogen (H₂) and carbone dioxide (CO₂). The damage is estimated by quantifying the surfacing fraction of cavities as a function of the observed area by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) after decompression. The structural analysis of the damaged samples under tension/decompression is compared to the structural analysis of the undeformed sample and to the one of samples having only seen a decompression. The comparison permits to separate the cavitation due to a mechanical effect from the one due to the gas decompression. The hydrogen effect is less detrimental than the carbon dioxide one, the latter increasing the nucleation of small cavities. On the other side, the tensile loading under gas pressure is more sensitive under hydrogen compared to carbon dioxide due to the plasticization effect in competition with the cavitation effect. The analysis gives a basis to the understanding of the damaging mechanisms by cavitation of the PVDF under thermo-diffuso-mechanical loading.

Keywords : Micro-cavitation, Diffusion, Tensile Loading, PVDF, TEM, SEM, H₂, CO₂

1 Introduction

Semi-crystalline polymers are known to exhibit cavitation damage when stretched above their glass transition temperature [1, 2], and particularly polyvinylidene fluoride [3, 4]. In a different way, the description of a gas dissolved in a polymer is receiving attention due to the special behaviour of these systems. Gas solubility in the host polymer, dilation of the host polymer and gas diffusion ability through the host polymer are properties that are obviously of interest. The gas-permeability as a function of pressure generally results in plasticization effect. Plasticization occurs when gas-concentration in the polymer is high enough to increase free volume and segmental mobility of the macromolecules. The free volume affects thermal, mechanical and relaxation properties, viscosity, diffusivity, among others [5, 6]. Solubility of gas, as carbon dioxide in polyvinylidene fluoride, was illustrated in some few works, for instance [7] and [8]. Only a few works considered relationships between gas sorption and mechanical behaviour, and yet, it is of high interest to accurately understand how damage processes like cavitation might interact with the diffusing fluid and be detrimental or not for the polymer. An example of detrimental coupling between gas diffusion and mechanics is the so-called “explosive decompression failure”. It refers to the cavitation occurring during decompression of a gas-saturated polymer. This type of damage has been studied in thermoplastics and rubbers exposed to different gases as carbon dioxide [7, 9], nitrogen [7] or hydrogen [10-12]. Gas interaction with the stretched polymer may have two antagonist effects. On the first hand, variations of the hydrostatic part of loading can help the expansion of the sorbed gas and promote cavitation. On the other hand, the amorphous phase plasticization associated with some gases can minimize the contribution of cavitation to accommodate the applied deformation. The aim of this work, focused on polyvinylidene fluoride, is to discuss these two antagonist effects of gas-polymer interaction by comparing cavitation occurring during tension in two gaseous environments: hydrogen and carbon dioxide.

2 Experimental

The tested material is a non-plasticized commercial alpha-poly(vinylidene fluoride) (PVDF) supplied in 3mm-thick extruded sheets (Kynar 4000). Its melting temperature is of 169.2 °C and its degree of crystallinity of 57 %. Carbon dioxide (CO₂) and hydrogen (H₂) were purchased from Air Liquid France and used without further purification. Tensile tests are carried out in an Instron 8802 tensile machine fitted with a pressure- and temperature-regulated chamber filled either by hydrogen or carbon dioxide. Samples are machined in the extrusion direction with a half scale ISO 527 shape. For each test condition, an additional undeformed sample is placed inside the chamber. It does not undergo any stretching but the same pressure cycle as the stretched one. The comparison of the “stretched” and “undeformed” series aims to separate damage nucleated under tension from that enhanced by the decompression stage. After fixing the sample and closing of the chamber, three nitrogen purges up to 1 MPa are successively processed to avoid mixture between the ambient air and the filling gas. The pressure chamber is then raised at 1 MPa min⁻¹ up to a constant value of 4 MPa which is maintained for one hour in order to equilibrate temperature at 30 °C (which is achieved about 20 min after the beginning of the pressure plateau) and to reach gas saturation of the sample. The time needed to reach saturation of the sample is estimated from the Crank’s solution of a one-dimensional Fickian diffusion problem through an infinite sheet [13]. The tensile test is then performed at a constant conventional strain-rate of 3.3 10⁻³ s⁻¹ and a regulated temperature of 30 °C, up to a maximal conventional strain of 20 %. The axial force, axial crosshead displacement, temperature and pressure are monitored during the test. Finally, the chamber is decompressed at 0.2 MPa.min⁻¹. Samples are cut from the tensile specimens with a razor blade then ultra-thin sections of about 60 to 80 nm in thickness are cut by ultramicrotomy performed in a Leica EM UC7-FC7 microtome at the temperature of -80°C with a Diatome diamond knife of 35 °, and observed with a Philips CM20 Transmission Electron Microscopy (TEM) operating at 200 kV. The surface of the truncated pyramids after the cutting of the ultra thin sections are observed with a JEOL 7000 Scanning Electron Microscopy-Field Emission Gun (SEM-FEG) operating at 7 kV.

3 Results

3.1 Tensile tests

Figure 1 shows the tensile stress-strain curves from tests performed in H₂ and CO₂. The slight stress decrease observed after yielding can be associated with a softening process which can correspond to the

cavitation process evidenced in the following. The maximum stress is reached at about 13 % of deformation and is slightly higher for the test in H₂ (56 MPa) than for CO₂ (53.5 MPa).

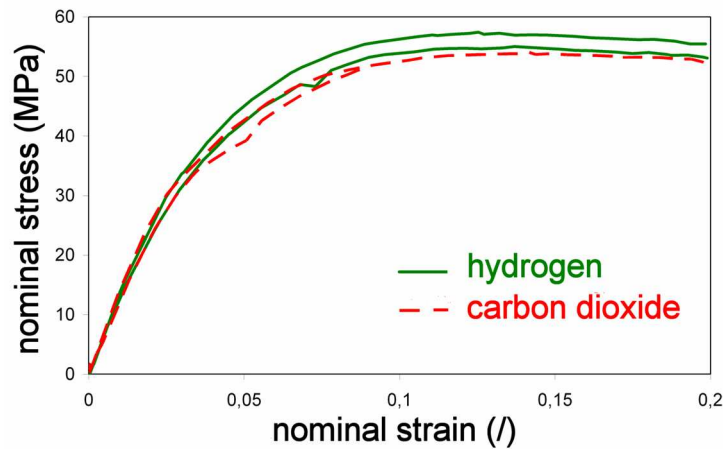


FIG. 1 – Tensile tests of PVDF in H₂ and CO₂, 30 °C and 4 MPa,.

3.2 SEM observations

Some typical SEM images of the as-received material as well as obtained after stretching in hydrogen and carbon dioxide are given in figure 2. Pre-existing cavities are observed in the as-received material, as very often encountered in this polymer due to the strong volume contraction upon crystallization during the process. SEM observations are made on the totality of the truncated pyramid that is a surface ranging from 5 000 to 11 000 μm^2 for the different samples. This first observation shows a cavitation that appears, at this scale, homogeneous in its spatial distribution as well as in size. This observation also allows a qualitative comparison between samples. For quantitative measurements of the cavitated surfaces, observations at a magnification ranging between 5 000 and 7 500 are performed on reduced surfaces. The size of the measured areas, ranging from 2 700 to 5 200 μm^2 , is given in Table 1. The measured area corresponds to the sum of all the surfaces taken into account for a detailed analysis on each sample. The number of cavities by surface unit in column 3 is obtained by the ratio between the total number of cavities seen at a magnification of 2 000 and the measured area. Column 4 corresponds to the percentage of the surface occupied by the cavities on the measured area. It will be established in the following that TEM surfaces are representative for damaged surface average. Since the total measured areas in SEM are much larger than in TEM, there are also representative with a much lower standard deviation estimated at 3 %. The corresponding scattering band is given into brackets.

SEM	Measured area (μm^2)	Number of cavities/ μm^2	Cavities surface percentage
As-received	2 743	0.016	0.080 % (0.078 % / 0.082 %)
H ₂ , 4 MPa, undeformed	5 218	0.014	0.114 % (0.111 % / 0.117 %)
H ₂ , 4 MPa, stretched	5 183	0.042	0.161 % (0.156 % / 0.166 %)
CO ₂ , 4 MPa undeformed	5 129	0.029	0.178 % (0.173 % / 0.183 %)
CO ₂ , 4 MPa, stretched	5 115	0.036	0.197 % (0.191 % / 0.203 %)

Table 1- Cavitation measured by SEM under different mechanical and diffusion environments.

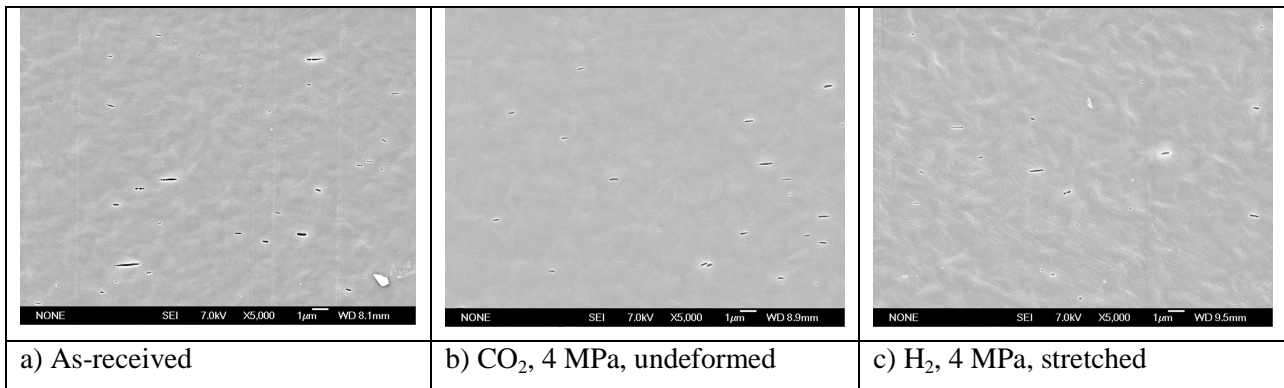


FIG. 2 - SEM images of PVDF samples after cryo-microtoming. The main direction of the plate or the tensile axis is horizontal in the pictures.

3.3 TEM observations

Some typical TEM images obtained after stretching or only a cycle of pressurization-decompression in hydrogen and carbon dioxide are given in figure 3. A few spherulites in micro-size are clearly distinguished. At such low magnification, micro-cavities elongated in the tensile direction (which is also the main direction of the plate) are well observed. At higher magnifications two additional populations of cavities are observed, i.e. a few spherical cavities with a mean diameter of 120 nm and very small bubbles of about 10 nm in diameter. The quantitative analysis of nano-bubbles needs higher magnification TEM observations of well contrasted ultra-thin foils which is beyond the scope of this study. Large cavities do not seem to be correlated to the spherulitic morphology (core or border). At a magnification of the same order as that used for SEM, the cavities appear similar in size and in distribution.

The damage results observed in the different samples are given in Table 2. Column 2 corresponds to the total area of the photos analyzed at a higher magnification, and column 3 corresponds to the percentage of surface occupied by the cavities with the scattering band given into brackets. The total measured area given in Table 2 is the sum of 5 to 15 individually analyzed photos, each of them corresponding to an area ranging between 20 and 200 μm^2 . The accuracy of the measurement is better in TEM due to the better contrast in transmission and to the higher magnification (from 10 000 to 50 000). But the total measured area in TEM is smaller than that measured in SEM and could be less representative. However a statistical analysis was done [14] showing that an area of 350 μm^2 is sufficient to obtain a standard deviation lower than $\pm 5\%$ and can be considered as a representative elementary surface for the analysis of the cavitation. Furthermore a double measurement and calculation of a same specimen leads to a deviation lower than 1 %.

TEM	Observed area (μm^2)	Cavities surface percentage
As-received	585	0.119 % (0.113 % / 0.125 %)
H ₂ , 4 MPa, undeformed	1 136	0.124 % (0.120 % / 0.128 %)
H ₂ , 4 MPa, stretched	381	0.199 % (0.179 % / 0.219 %)
CO ₂ , 4 MPa, undeformed	1 183	0.307 % (0.301 % / 0.313 %)
CO ₂ , 4 MPa, stretched	1 049	0.375 % (0.368 % / 0.382 %)

Table 2 - Cavitation measured by TEM under different mechanical and diffusion environments.

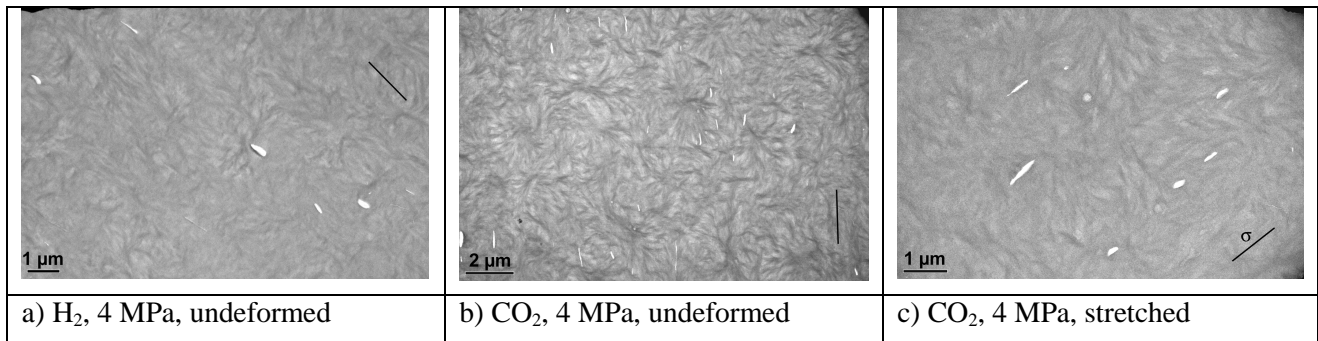


FIG. 3 - TEM images of PVDF ultra-thin sections. The line in the pictures indicates the main direction of the plate or the tensile axis.

4 Discussion

Figure 4 summarizes the cavities surface fraction estimated from SEM and TEM micrographs, respectively, in the different testing conditions. A first analysis shows similar evolutions between TEM and SEM. However, the cavities surface percentage estimated from TEM observations is always higher than that obtained from SEM micrographs, probably because some cavities are not visible at the lower SEM magnification and also because the cavities contrast is better in transmission microscopy. It is also possible that the stress relaxation occurring around the cavities during microtomy of the ultra-thin foils increase their size compared to that existing in the bulk material.

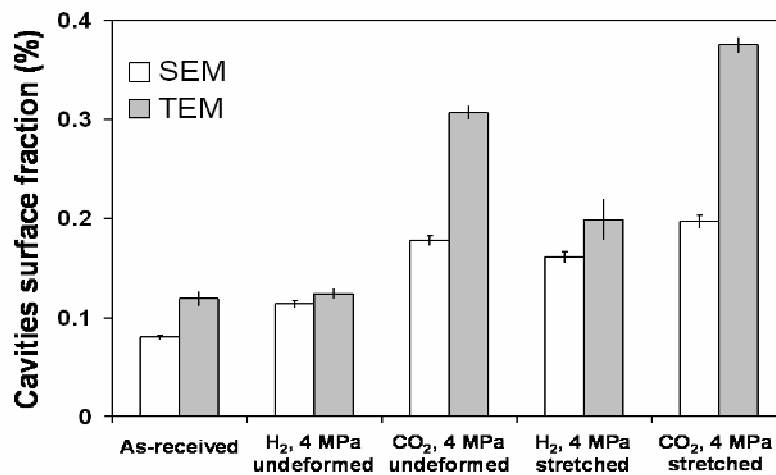


FIG. 4 - Cavities surface fraction estimated from SEM and TEM observations in the different testing conditions. Scattering bands depend on the observed area.

Both the tension and decompression stages affect the hydrostatic stress and can be responsible for the observed damage. Let us focus first on the influence of decompression by comparing the as-received sample to the undeformed ones, the latter undergoing only the gas cycle and especially the decompression. Decompression in hydrogen does not enhance any significant damage, especially considering TEM results. Indeed, the cavities surface fraction measured from TEM micrographs after decompression from 4 MPa in H₂ is only 4.2 % larger than in the as-received material which is about the scatter value (5%). Unlike in H₂, decompression in CO₂ appears very detrimental. Indeed, after decompression from 4 MPa in CO₂, the cavities surface fraction of the as-received material is multiplied by about 2.2 and 2.6, when estimated respectively by SEM and TEM. The influence of tension can be pointed out by comparing the “undeformed” samples to the stretched ones. In this case, both series undergo the decompression stage. After tension and decompression in H₂, the damaged surface is significantly larger than in the undeformed samples, i.e. 41 % (SEM) and 60% (TEM). Since the difference between undeformed and stretched samples is higher in TEM, it can be supposed that the small cavities population is favoured. Damage observed in SEM micrographs

after tension in CO₂ is only slightly higher than that observed in samples stretched in H₂. For the same pressure, the damaged surface fraction is larger by 22 %. The difference is more marked in TEM micrographs, with a damaged surface fraction in CO₂ exceeding by 88 % that measured in H₂. This may suggest that tension in CO₂ promotes nucleation of small cavities compared to that nucleated in H₂.

The second important result of this series deals with the limited increase of cavitation enhanced by CO₂ during the tension stage itself. Indeed, the relative increase of damage surface fraction between undeformed and stretched samples in CO₂ is 11 % in SEM micrographs and 22 % in TEM ones. This can be regarded as a consequence of the plasticizing effect of CO₂: the increased molecular mobility makes the cavitation contribution less necessary to accommodate the applied deformation, in the same way as observed in air when increasing the temperature. From the present results, it is difficult to discuss the relative influence of the growth of pre-existing cavities compared to the nucleation of smaller ones. No observation suggests the germination of smaller cavities because of CO₂ plasticization. At relatively low pressure, energetic interactions were observed in CO₂/PVDF systems [7]. This was favoured by the presence of high polar C-F bonds in PVDF leading to dipolar interactions with CO₂ [15].

5 Conclusion

Tensile tests were performed on a semicrystalline alpha-poly(vinylidene fluoride) in hydrogen and carbon dioxide atmospheres. The damaged surface fraction was estimated from SEM and TEM micrographs after decompression and compared to the as-received material and to samples submitted to gas decompression only. It was checked that the observed surface area was representative for both microscopy devices. Decompression in hydrogen appears to have only a slight effect on cavitation and appears much less detrimental than carbon dioxide, which is bound to enhance small cavities nucleation as attested by the difference between SEM and TEM results. On the other hand, tension under gas pressure is more sensitive to hydrogen compared to carbon dioxide, due to plasticizing effect in competition with cavitation in this latter gas.

This experimental status constitutes a contribution to the understanding of micro-mechanisms of gas sorption on damage nucleation of semi-crystalline polymers during coupled diffuso-mechanical damage.

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