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Mechanochemical degradation of poly(vinyl fluoride) by sodium hydroxide measured by microindentation

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Abstract The degradation of the mechanical properties of deformed PVDF during its mechanochemical ageing in sodium hydroxide (soda) was followed by microindentation measurements, especially the local reduction of the elastic modulus and the hardness. This allows measurements on a local scale of the mechanical properties on the surface and in-depth as a function of the strain level and the ageing time. Microindentation tests with Berkovich indenter have been performed with a Nanoindenter XP® (MTS). Measurements are made at penetration depth less than 2 μm for an applied load of 10 mN. During ageing in soda (Ph 14) at 90 °C up to 16 days, various deformations ε (0, 22 and 38%) are imposed on PVDF tensile specimen. For the first two imposed deformations ($\varepsilon = 0$ and $\varepsilon = 22\%$), mechanical degradation is limited to some percent (less than 7%). For the greatest deformation ($\varepsilon = 38\%$), mechanical degradation continues to decrease with ageing time (more than 21%). Microindentation tests show that a range of low deformations exists in which the mechanochemical degradation is limited and no limitation is observed for larger imposed deformation.

Introduction

Poly(vinyl fluoride) (PVDF), the homopolymer of 1,1-difluoroethylene($(CH_2{=}CF_2)_n$), is a tough engineering thermoplastic with a high molecular weight semi-crystalline polymer with high degree of crystallinity (52%). It forms spherulites which can reach a size of more than 100 μm under certain conditions of crystallizations [1]. PVDF belongs to the family of the fluorinated polymers which is characterized by high thermal stability, exceptional outdoor weather resistance due to its total inertness to UV radiation, offers very good chemical resistance in the presence of a wide variety of different chemicals and solvents up to high temperatures of approximately 150 °C, mechanical strength and toughness, behaviour with fire and weak generation of smoke, some piezoelectric and pyroelectric properties etc. Thus, PVDF has the characteristic stability of fluoropolymers when exposed to harsh thermal, chemical and ultraviolet environments while retaining the properties of a conventional thermoplastic material.

Most previous studies showed that PVDF has an excellent resistance to abrasion and most chemicals [2, 3]. Strained PVDF samples were exposed to concentrate sulphuric acid (98%) for a period of 28 days at 80 °C, other strained PVDF samples were heated in air for 28 days at 80 °C. No signs of chemical attack or cracking were observed on stressed samples exposed to concentrated sulphuric acid or subjected to days heating in air at 80 °C. However, the PVDF like most of engineering thermoplastics are susceptible to chemical and physical degradation which is strongly affected by temperature, level of mechanical deformation and environmental conditions. Under a combined action of mechanical stresses, chemically aggressive environment of high pH sodium hydroxide and high temperature (90 °C), the damage in PVDF

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resulting from mechanochemical degradation is usually manifested as discolouration of the samples due to dehydrofluorination [4, 5]. At a certain level of chemical embrittlement of material [6], formation of microcracks was frequently observed within a layer of exposed surface of degraded polymer. Indeed, failure of PVDF has occurred in the form of cracking of sheet and weldments in chemical environments that were not expected to cause problems. There have been reported failures (cracking) of PVDF pipes and storage tank linings in soda in the temperature range from 50 to 90 °C, in particular on the level of the weldings.

It is then of practical interest to study of effects of mechanochemical degradation of PVDF on its mechanical properties. More precisely, it relates to the embrittlement of the PVDF in chemically aggressive environment of warm soda in the presence of mechanical strain by 'stress corrosion cracking' (SCC). Many studies on SCC of polymers have been published [2–4, 7–12]. Some papers [11, 12] explain this phenomenon mainly in terms of solvent diffusion, whose penetration is accounted for based on the solubility parameter concept. According to other reports [2, 8], SCC is often coupled to chemical degradation between the penetrating solvent and the polymer, and the applied strain accelerates the diffusion of the chemical and then the discoloration. Specifically, the behaviour of PVDF in alkaline sodium hydroxide solutions has been investigated in the past [2–6, 8]. In these studies, the general mechanism of soda chemical attack on PVDF relies on the reaction of dehydrofluorination, the formation of conjugated C=C bonds and the inclusion of oxygen functionalities on surface treatment [4, 5], causing reddish brown colouration in the area of degradation [8]. Evidence has been presented in a preceding study [3] to indicate that the hostility of the NaOH environment increases above pH 13 but then decreases at higher values, suggesting a maximum effect at pH values of about 13.5–14.

The main aim of this work is to establish the relation between the ageing time of mechanochemical degradation of PVDF by the soda at 90 °C and the level of the imposed mechanical deformation. Using microindentation technique we will emphasize the microscopic evolution of PVDF mechanical degradation directly on the surface and in-depth. Microindentation allows measurement, with the local scales of spherulites, some mechanical properties on the surface like the local reduced elastic modulus E^* and of hardness H [13].

Experimental

An experimental procedure was developed in our laboratory. It makes possible to impose on tensile specimen variable mechanical deformation during their ageing in a molar warm sodium hydroxide solution (pH 14) over a period of 16 days. Then, the mechanical properties have been estimated using a nanoindentation XP® (MTS) apparatus equipped with a three-sided pyramidal Berkovich indenter. Measurements are performed at penetration depth less than 2 µm for an applied load of 10 mN. PVDF tensile specimen used in the experiments was machined from injection moulded plaques of 4 mm thickness and the edges were polished with increasingly finer grades of grinding paper to reduce the effects of surface defects and machining.

Mechanochemical degradation of poly(vinyl fluoride) by sodium hydroxide test

An aqueous solution of sodium hydroxide was made up by dissolving 40 g of pellets in distilled water to make 1 M NaOH with a pH value of 14. All mechanochemical ageing tests were conducted in this solution at 90 °C up to 16 days. During the ageing test, a constant deformation was imposed on the tensile specimen using a stainless device, illustrated in Fig. 1, rectangular assembly (30 × 60 mm) of 3 mm thickness, provided with two bars with screws offer a good fixing of the tensile specimen.

The tensile specimen is drawn by the INSTRON 4500 machine to a given value of deformation with a deformation rate of 1 mm/min (3.10^{-4} s^{-1}). One fixes well the device around the central zone of the tensile specimen, setting an imposed deformation. A PolyTetraFluoroEthylene (PTFE) or Teflon® film is placed in several layers on the part of surface to protect some chosen parts against the chemical attack of soda. Another stainless device is then used to maintain the PTFE film via a part in PVDF. The

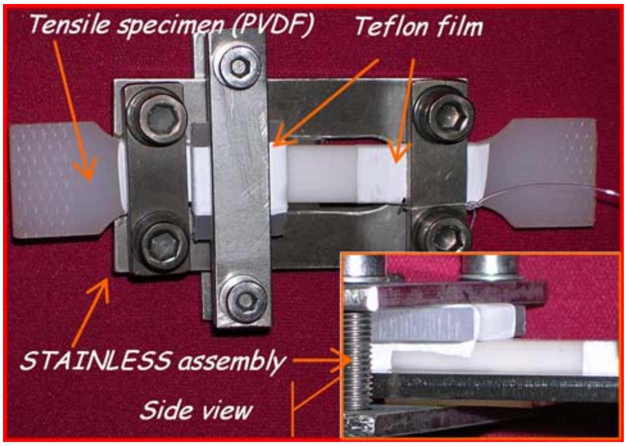


Fig. 1 Experimental device used for maintaining a fixed deformation of tensile specimen boundaries during its ageing in sodium hydroxide. Parts of the specimen surface are protected against sodium hydroxide by a polytetrafluoroethylene (PTFE) or Teflon® film

tensile specimens with various imposed deformation ε (0, 22 and 38%) are then aged in soda (pH 14) at 90 °C with part of surface of 5 mm broad initially protected. They are left from the ageing reactor at several times (8 h, 20 h, 4 days and 16 days). Each time, surface previously protected is widened by 5 mm and the specimen is replaced for ageing continuation. Consequently, we form on each tensile specimen a succession of surfaces aged at various times. At the end of ageing time, the tensile specimens are left cool with room temperature before washing them with distilled water to eliminate soda; they are released from the stainless devices. They are let dry with room temperature during at least 3 days to eliminate the liquid absorbed by the specimen.

Then, a series of measurements of the reduced elastic modulus E^* and hardness H are programmed by microindentation on the precedent succession parts of protected surfaces of these tensile specimens to evaluate the mechanical degradation of the PVDF.

The microindentation test

The macroscopic traditional techniques of mechanical properties are not really adapted to detect possible microscopic fluctuations on these properties or variation from surface to depth of a specimen. In the microindentation test, the length scale of the specimen penetration is measured in nanometres; this makes it a technique particularly adapted to our study of the surface mechanical degradation of the PVDF during mechanochemical ageing in the sodium hydroxide. It allows the local microscopic identification of the deterioration of the mechanical properties responsible for SCC phenomenon. This experimental technique is increasingly used to reach the mechanical properties (elastic module, hardness…) of surfaces or ultrathin layers with nanometre thickness and has been successfully used for metals [14, 15].

The indentation load (P) is determined as a function of penetration depth of the indenter into the specimen surface (h) [13, 16, 17] (Fig. 2).

The loading part of the indentation cycle consists of an elastoplastic deformation. A reduced elastic modulus E^*, which represents the elastic response of material, is determined from upon unloading slope S of load-deformation curve using the Oliver–Pharr method [13, 16, 17] and by assuming a linear purely elastic behaviour

$$S = \left(\frac{\mathrm{d}P}{\mathrm{d}h}\right)_{h_{\max}} \approx \frac{2\beta}{\sqrt{\pi}} E^* \sqrt{A} \tag{1}$$

where β is a parameter related to the indenter geometry and A is the projected contact area indenter/material. The hardness H, which represents the resistance of material to its penetration, is equal to maximum applied load $P_{\max}$ divided by A

$$H = \frac{P_{\max}}{A} \tag{2}$$

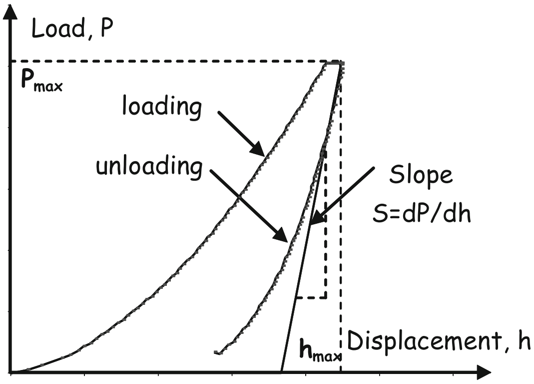


Fig. 2 Loading–unloading curves during Berkovich microindentation standard test [18]

However, even if this technique has great advantages, curves can sometimes be difficult to analyze for time dependant materials like polymers. First reason lies on the non uniformity of the stress, strain, and strain rates fields coupled with the non linear response of the material. Second reason lies on the time dependency of viscoelastic and viscoplastic materials and so the retarded response due to creep and relaxation. Thus, the measurements of E^* and H of polymers carried out by microindentation cannot be considered a priori as absolutes corrects measurements in comparison with linear elastic and perfectly plastic time independent materials.

Nevertheless, microindentation experiments on PVDF can be conveniently used for the relative comparisons considering the evolution in time of the mechanochemical degradation for given mechanical deformation levels. The mechanochemical ageing of the PVDF by soda is then carried out on the surface of contact between the two mediums (the PVDF plate and the soda solution) for some micrometers of depth in the specimen [19].

During Berkovich microindentation tests presented here, successive three cycles of load–hold–unload cycles were carried in order to obtain value for three different depths, as shown in Fig. 3. The maximum loads were fixed at 2.5 mN for cycle 1, 5 mN for cycle 2 and 10 mN for cycle 3. The loading and unloading rate was set at 167 μN/s. A hold time (5 s) with constant load is also carried out before the unloading in order to minimize the time depending mechanisms.

At each location, nine indentations were systematically processed in order to inform about possible scattering of such local microscopic test. These points of measurement

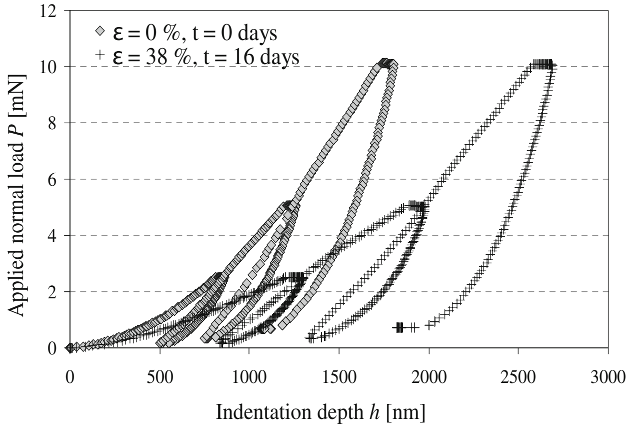
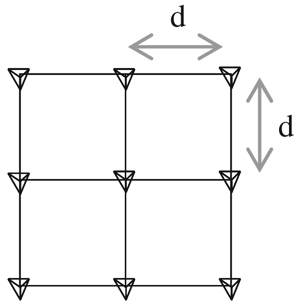


Fig. 3 Three cycles of load–hold–unload versus indentation depth for a typical Berkovich microindentation test with successive maximum loads of 2.5 mN (cycle 1), 5 mN (cycle 2) and 10 mN (cycle 3) in a PVDF surface through imposed deformation 0% (*resp.* 38%) and ageing time 0 day (*resp.* 16 days)

Fig. 4 The 9 points measurement distribution for a microindentation test



set out again on centred square with distance $d = 75$ µm between two indented points (Fig. 4).

Generally, the indentation leaves residual stresses in material around the centre of the imprint after the unloading phase. The distance, *d*, between the indents points must be sufficiently important so that other measurements are not disturbed and do not interact by this residual stress and strain fields. Knowing that the measured imprint size is approximately 5 µm, the distance, *d*, between two successive indentation in the two plane direction was chosen to be 15 times the imprint size $d = 15 \times 5$ µm.

Considering Berkovich test, the strain rate $\overset{\circ}{\varepsilon}$ during the loading phase is given by $\overset{\circ}{\varepsilon} = \frac{\overset{\circ}{h}}{h}$ [20, 21]. It should be noticed that, taking into account the limitations in load control of the machine of microindentation, currently the tests are carried out with controlled force. It was then not possible to maintain constant $\overset{\circ}{\varepsilon}$. A mean value of the strain rate can be estimated by the ratio

$$\overset{\circ}{\varepsilon} = \frac{\mathrm{d}(\ln h)}{\mathrm{d}t} \qquad (3)$$

In this study, this strain rate is estimated at 16.10^{-3} s^{-1} and follows small variations ($\pm 1.10^{-3}$ s^{-1}) from one test to another. Consequently, it can be considered that the reduced elastic modulus was measured at quasi-constant loading rate [18].

Experimental results

Figure 5 shows the variation of the reduced elastic modulus *E** and hardness *H* versus mechanochemical ageing time in soda (pH 14) at 90 °C for the imposed deformation level 38%. It is noticeable that the values of *E** and *H* determined with second and third unload-cycle (the maximum loads are, respectively, 5 mN and 10 mN) do not have present significant differences compared to those measured with the first unload-cycle (the maximum load is 2.5 mN). This indicates that the experimental values of *E** and *H* do not vary significantly with depth at least for depths up to 2.5 µm.

Then, in the sake of simplicity, we represent in Fig. 6 only the values of *E** and *H* determined with the first unload-cycle. This illustrates the variation of the reduced elastic modulus *E** and hardness *H* versus mechanochemical ageing time in soda (pH 14) at 90 °C for three imposed tensile deformation levels 0%, 22% and 38%.

In Fig. 6 and for each ageing time, the averages values of *E** are represented and *H* with the standard deviations of nine indentations. It is noticeable that

- For 0% (*resp.* 22%) of deformation level: a reduction of 3% (*resp.* 4%) of *E** and 4% (*resp.* 7%) of *H* is reached at the end of 24 h (*resp.* 8 h) of time ageing on a depth of 0.9 µm, this degradation remains stable and does not move any more up to 16 days. No discoloration and no microcracks are observed on surface.
- For 38% of deformation level: the reduced elastic modulus *E** and hardness *H* continue to decrease with the ageing time and after 16 days the reduction reaches 21% and 25%, respectively. Reddish brown colouration is observed on the 16th day. Degradation area and microcracks have been formed on the surface of the test specimens perpendicularly to the tensile direction.

It should be noticed here that the entire test specimens, both protected by PTFE film parts and not protected parts, are set to age in soda at 90 °C. The protected parts do not undergo chemical ageing by soda, but they all undergo the same physical ageing phenomena due to temperature.

Figure 7 represents the photographs taken by the optical microscope of the microindentation machine directly after the test. They show the residual imprints left by the Berkovich indenter on a surface of PVDF aged 16 days in soda with pH 14 at 90 °C, with imposed deformation of 22%

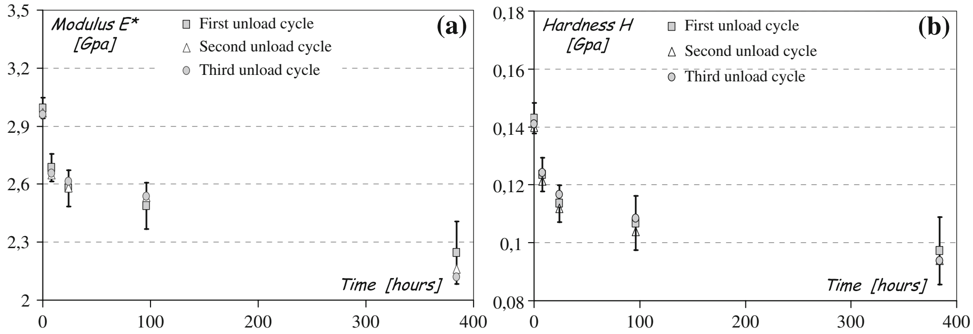


Fig. 5 Degradation of mechanical properties **a** reduced elastic modulus E^* and **b** hardness H of PVDF by mechanochemical ageing in sodium hydroxide (pH 14) at 90 °C according to the imposed deformation level 38% versus ageing time. Measurements were carried out by standard microindentation Berkovich test with maximum loads of 2.5 mN (first unload cycle) 5 mN (second unload cycle) and 10 mN (third unload cycle)

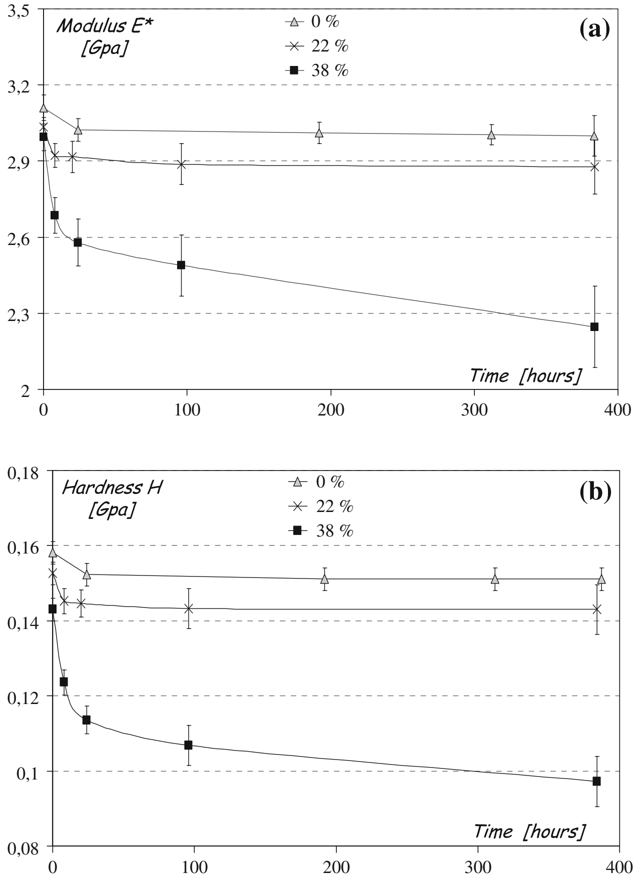


Fig. 6 Degradation of mechanical properties **a** reduced elastic modulus E^* and **b** hardness H of PVDF by mechanochemical ageing in sodium hydroxide (pH 14) at 90 °C according to the imposed deformation levels (0, 22 and 38%) versus ageing time. Measurements were carried out by standard microindentation Berkovich test with maximum load of 2.5 mN on a depth of less than 1 μm

(Fig. 7a) and 38% (Fig. 7b), the imprints diameters are, respectively, 2.1 and 5 μm. The imprint kept the same geometry as the indenter point of three-side pyramidal form. Microcracks have been formed on the surface of the surface test specimen perpendicularly to the direction of traction.

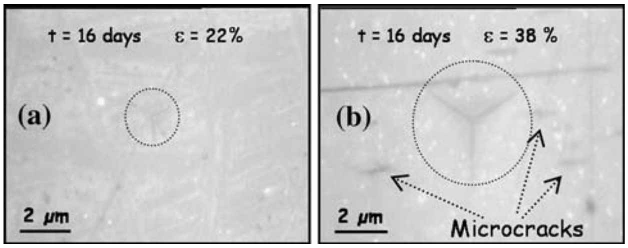


Fig. 7 Residual Berkovich shape imprints of indentation in a 16 days PVDF surface aged in soda pH 14 at 90 °C for an imposed deformation of 22% (**a**) and 38% (**b**). The maximum indentation loads was 10 mN

The residual imprint of the right-hand photograph is larger in size than that of left one, the applied load, 10 mN, being the same for both tests. This increase in size comes principally from a reduction of the hardness H and a more important indentation depth for a given load for a less hardness. The measured indentation depths are 1.8 μm for Fig. 7a and 2.7 μm for Fig. 7b. The reduction measured in the hardness H is more important for 38% compared to 22% of imposed deformation; these reductions being, respectively, 25% and 7%. These reductions shows that the material becomes significantly softer during ageing time if initially deformed more than 22%. The decrease in the reduced elastic modulus is not directly linked to the imprint size since elasticity does not involve residual strains. On the other hand, it is obvious that a variation of the yield stress, σ_y, can be responsible for a hardness variation. Nevertheless, considering the geometry of a Berkovich indenter, it is expected that the imprint size could also be related to fracture toughness. Indeed, the shape of a Berkovich tip of angles 142.3° can generate notches in front of the indenter.

Discussion

The microindentation measurements of the E^* and H reveal that an asymptote in mechanical degradation is reached at the end of few hours of ageing process for none or little deformed PVDF test specimens. This reveals the existence of an auto-inhibition process of the mechanochemical degradation mechanism. We can try to explain it by the formation of impenetrable layer of reaction products of PVDF with the soda. Evsyukov et al. have already proposed the formation of such a protective layer [22]. The chemical reaction products have a density lower than that of PVDF [23]. Thus, it is plausible that they could form a protective layer preventing the diffusion of soda in polymer and stops its chemical and mechanical degradation.

The increase of the degradation is little for an imposed deformation of 22% and relatively important for imposed deformation of 38%. The additional mechanical deformation, taking place with the passage of imposed deformation from 22% to 38%, seems indeed to force part of the crystalline phase and the amorphous phase of the material to be parallel to the tensile direction as envisaged in the fibrillary structure model [24].

It is expected that this orientation slows down the diffusion of soda in the PVDF [11, 25]. But a reduction in the diffusion goes against the observed increase in mechanical degradation and consequently cannot explain it, quite to the contrary. On the other hand, the transformation of crystalline phase ($\alpha \rightarrow \beta$) by mechanical deformation is known to occur at a level of deformation about 38% [26–29]. This phase β could have a more important chemical reactivity with soda and it could cause this increase of mechanical degradation.

Conclusions

In spite of the difficulties related to the analysis of the microindentation tests on visco–elasto-plastic materials, our results shows, thus, that the microindentation of PVDF at room temperature is a convenient technique particularly appropriate for studying the mechanical degradation. The elastic modulus and hardness for a depth of measurement equal to 2 μm have been successfully measured during mechanochemical ageing in the sodium hydroxide (pH 14) at 90 °C. A direct relationship was observed between the mechanical degree of degradation and the mechanical deformation level. It is shown that above 22% of deformation the elastic modulus and hardness reduce only for a few percent in the first day of ageing and remain almost constant up to 16 days. Below 38% of deformation, the elastic modulus and hardness continue to decrease with the ageing time and after 16 days the reduction reaches 21% and 25%, respectively.

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